



# Acquisition Directorate

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## Research & Development Center

Report No. CG-D-04-17

# Underwater Sediment Sampling Research

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January 2017



# Homeland Security

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# Underwater Sediment Sampling Research

## Technical Report Documentation Page

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### EXECUTIVE SUMMARY

The USCG R&D Center sought to develop a bench top system to determine, in situ, the amount of total petroleum hydrocarbons (TPH) in underwater bottom sediment. As a bench top system, this design would not have met all of the final requirements needed for a fully deployed system, but the concept allows preliminary evaluation in a laboratory setting. This scenario can occur whenever oil is weathered and mixed with silt or sand. The result is that the oil sticks to the silt and sinks to the bottom. Poles were used to agitate the bottom during the Kalamazoo River spill in 2010; and the detection measure of the oil locations was whether sheening did or did not occur. Currently, the only reliable method to determine the exact oil concentration is to obtain a full sample. During the Deepwater Horizon spill response, a large amount of samples were needed because oil only comprised about 10-20 percent of the tar mats and were sometimes very scattered.

Oil production from the Canadian Oil Sands project in Alberta, Canada has led to a new type of crude oil-like product composed of bitumen and added diluents (diluted bitumen or Dilbit). Furthermore, the increased movement of Dilbit by rail and pipeline raises questions concerning the proper approach to spill response for this new product, and the few freshwater/marine spills that have occurred to date have not provided sufficient experience to resolve these questions. The United States Coast Guard (USCG) Research and Development Center (RDC) initiated the current study to design, construct, and test of a bench top system to sample an oil/sediment mixture in situ, and measure the concentration of total petroleum hydrocarbons (TPH). While this study focuses on Dilbit and a Texas crude, a sampling process that could also be applied to other types of oils and conditions is highly desirable.

The test team developed a Sediment-Oil Measurement System (SOMS) as a bench top prototype. The RDC has set operational parameters for a fieldable system as follows: function at depths of up to 100 feet, in currents of up to 0.5 knots, and perform at least five (5) samples per hour during a 12-hour operating window without bringing a sample to the surface.

The methodology used in this study was based on the hypothesis that the TPH content of a submerged oil/sediment mixture is quantitatively related to the concentration of TPH measured in the interstitial waters (i.e., pore water). The result was not an exact concentration of oil in the sediments, but a preponderance of evidence about the amount of oil at that location. The test team used a fluorescence oil sensor (Turner Designs Cyclops-7), enclosed in a novel probe designed for this study, to measure the TPH contained in known submerged oil/sediment mixtures; called a Sediment-Oil Measurement System (SOMS). The team validated the measurements using an independent method (Dexsil PetroFlag TPH Test Kit). The data generated from this effort was used to develop mathematical relationships that could be applied to measuring TPH in real world submerged sediments.

Two significant obstacles were encountered:

1. The unusual hydrophobic nature (stickiness) of the Dilbit made preparing calibrated oil/sediment/water mixtures extremely difficult; and innovative mixing procedures were developed to overcome this.
2. Once prepared, the calibrated mixtures did not remain stable over the timeframe of the testing (2-4 months); resulting in unexpected readings over time, particularly for higher concentration Dilbit mixtures. The unexpected results were resolved through further experimentation.



## Underwater Sediment Sampling Research

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Using Texas Raw Crude and Dilbit, the study demonstrated a successful bench top prototype system that could potentially be further developed for deployment on an ROV, and which appears to meet the operating criteria described above for different types of oils. More work is needed (a) to evaluate the usefulness of this type of data, (b) to develop a process that addresses the calibration required, and (c) to determine the type of environmental conditions and oils for which this can be used. In addition, this report describes a shallow water variation of a fieldable SOMS that might serve as a next step in the development of this technology.



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### LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

|                    |  |
|--------------------|--|
| ABS                | Acrylon butadiene styrene                      |
| ADC                | Analog-to-digital converter                    |
| API                | American Petroleum Institute                   |
| CONOP              | Concept of operation                           |
| COTS               | Commercial-off-the-shelf                       |
| CSV                | Comma separated value                          |
| DB                 | Diluted bitumen                                |
| Dilbit             | Diluted bitumen                                |
| EPA                | Environmental Protection Agency                |
| m                  | meter  |
| mm <sup>2</sup> /s | Millimeter squared per second                  |
| mg/L               | Milligrams per liter                           |
| MS                 | Microsoft                                      |
| PAH                | Polycyclic aromatic hydrocarbon                |
| ppm                | Parts per million                              |
| RDC                | Research & Development Center                  |
| ROV                | Remotely operated vehicle                      |
| SAIC               | Science Applications International Corporation |
| SBC                | Analog-to-digital converter                    |
| SME                | Subject matter expert                          |
| SOMS               | Sediment-oil measurement system                |
| SubChem            | SubChem Sensor Systems, Inc.                   |
| TPH                | Total petroleum hydrocarbons                   |
| TR                 | Texas Raw Crude                                |
| U.S.               | United States                                  |
| USB                | Universal serial bus                           |
| USCG               | United States Coast Guard                      |
| WAF                | Water accommodated fraction                    |
| WTI                | West Texas Intermediate crude oil              |



# 1 INTRODUCTION

## 1.1 Background

In certain conditions during an oil spill, the oil is mixed with silt at the bottom of a body of water and it becomes difficult to find. This situation can occur whenever oil is weathered or mixed with silt or sand due to turbulence. The result is that the oil sticks to the silt and sinks to the bottom. Poles were used to agitate the bottom during the Kalamazoo River spill in 2010 and the measure of the oil locations was whether sheening did or did not occur. Currently, the only reliable method to determine the exact oil concentration is to obtain a full sample. During the Deepwater Horizon spill response, a large amount of samples were needed because oil only comprised about 10-20 percent of the tar mats and can be very scattered.

There has been an increase in the movement of products from the Canadian Oil Sands project in Alberta, Canada. This includes shipment by rail and pipeline of Dilbit, which is a crude-like oil that is composed of bitumen (Figure 1) and added diluents (diluted bitumen), deriving the shortened term “Dilbit.” Although the characteristics of Dilbit are in some ways similar to other crude oils, the combination of heavy components with a lighter crude or condensate raises questions about its behavior and approaches to spill response. The few freshwater/marine spills that have occurred to date for this type of product have not provided sufficient experience to answer these questions. The United States Coast Guard (USCG) Research and Development Center (RDC) is seeking a method to sample this sunken mixture and analyze it in situ. While this background focuses on Dilbit crude, a sampling process is needed for all types of oils, such as detecting the tar mats that were created near shore during the Deepwater Horizon oil spill. Therefore, the process sought in this study should ideally be usable for other types of oil in addition to Dilbit.



Figure 1. Bitumen, which can be diluted to become Dilbit crude oil.

## 1.2 Scope

The purpose of the current project was to design, construct, and test a bench top Sediment-Oil Measurement System (SOMS) consisting of equipment and a process to sample an oil/sediment mixture, and measure the concentration of total petroleum hydrocarbons (TPH). Once designed, the proof-of-concept for the system would take place in a laboratory demonstration sometimes described as a “Bench Top” system.. After successfully demonstrating the system, the objective was to develop recommendations for adapting the technology and process to function in a final working system that could be mounted on a remotely operated vehicle (ROV) for test purposes. A final working system would need to function at depths of up to 100 feet,

in currents of up to 0.5 knots, and perform at least five (5) samples per hour during a 12-hour operating window without bringing a sample to the surface. These initial requirements are based on the experience from previous spills.

Recent studies have attempted to better understand the oil/sediment mixing process (Environment Canada, 2013; Fitzpatrick et al., 2015; Sammarco et al., 2013). In addition, documentation of the response to the Kalamazoo River in 2010 provides additional description of the problems encountered (Dollhopf and Durno 2011, Dollhopf et. al. 2014). These studies may help achieve the laboratory goal of producing sediment samples with a range of known TPH contents for use in testing. Studying how and why such mixtures occur in the environment were, however, beyond the scope of this project.

### 1.3 Project Team Members

The project team included SAIC, as the prime contractor to the RDC, and SAIC's subcontractor, SubChem Sensor Systems, Inc. (SubChem). SubChem provided in situ sensor and analysis expertise, as well as the use of their engineering and chemical oceanography laboratory spaces. SubChem is located on the University of Rhode Island Oceanography Campus in Narragansett, RI. The project support team included the following personnel.

- **Science Applications International Corporation:**
  - Robert Young, Project Manager.
  - Michael Morin, Electrical Engineer.
  - Brian Hannigan, Mechanical Engineer.
- **SubChem Sensor Systems, Inc:**
  - Alfred K. Hanson, President, Chemical Oceanographer, and In situ Chemical Analysis Subject Matter Expert (SME).

## 2 LABORATORY TEST SET UP

The experimental research and laboratory proof-of-concept demonstration was performed at SubChem during the period February through June 2016; therefore all test dates are 2016. The overall methodology involved using a fluorescence oil sensor (Turner Designs Cyclops-7) to measure the TPH contained in the interstitial waters (i.e., pore water) of known submerged oil/sediment/water mixtures. This approach is based on the new hypothesis that the TPH content of a submerged oil/sediment mixture is quantitatively related to the concentration of TPH measured in the pore water. This means that a specific number for the oil concentration is not being determined but the higher hydrocarbons in the water will provide a preponderance of evidence that oil is at that location. The following challenges were encountered:

- building a set of calibrated oil/water/sediment mixtures for comparison with the Cyclops-7 sensor measurements;
- using an independent method (PetroFlag TPH Test Kit) to validate the sediment oil concentrations;
- developing a probe to house the oil sensor, allow it to penetrate the sediment layer, and provide for water flow past the sensor while screening out sediment;
- providing a data recording system; and
- devising a repeatable sampling/measurement process.

The methodology is discussed further in the following subsections. A high-level schematic diagram of the lab setup is shown in Figure 2.

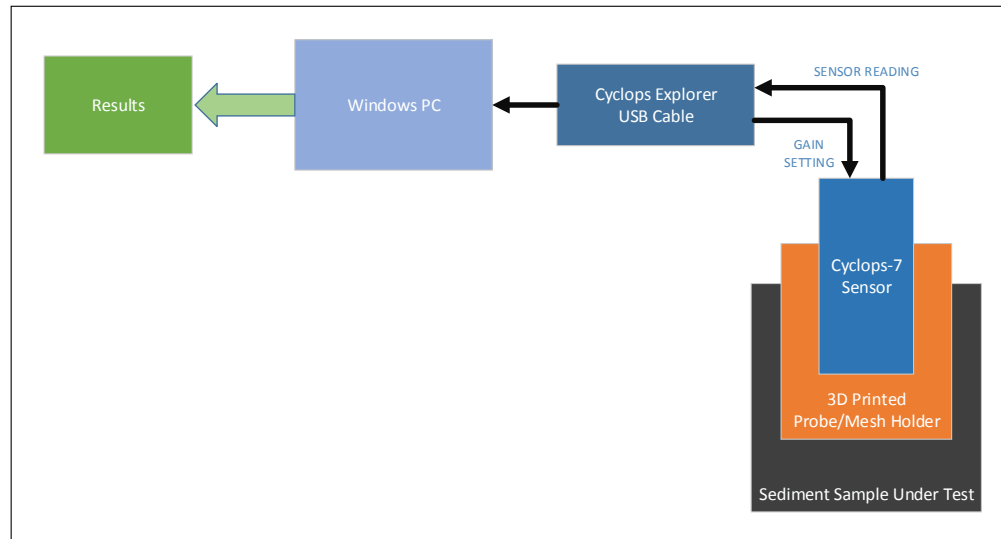


Figure 2. Laboratory test setup.

### 2.1 Mixing and Calibration of Oil/Sediment/Water Mixtures

In the lab, SubChem prepared a TPH concentration gradient of 17 well-mixed oil/sediment/water samples (Figure 3), contained and mixed in 8-liter clear plastic laboratory containers. The mixtures included three controls (no oil), six with Texas Raw Crude, and eight with Dilbit. APPENDIX A provides information about the general characteristics of these oils. To prepare the mixtures, the oil was combined with a known quantity of fine-grained sand covered with a layer of natural freshwater or seawater. For independent validation, SubChem determined the TPH content of these prepared oil/sediment/water mixtures using a solvent extraction-emulsion turbidity field test kit (Dexsil PetroFlag) that has been verified by the U.S. Environmental Protection Agency (EPA) for measuring TPH in soils (Figure 4) (U.S. EPA, 2007, 2001).



Figure 3. Seventeen experimental containers (photo taken 31 May).





Figure 4. Dexsil PetroFlag field test kit.

After an equilibration period of two days, the crude oil content of both the supernatant water and the sediment pore waters of the test samples were measured in situ using the Cyclops-7 oil sensor probe described in the following section. The measurements were compared to the known TPH contents of the oil/sediment/water mixtures, and used to calibrate and evaluate the sensor probe. These measurements were collected from samples of Dilbit crude oil obtained from Enbridge, Inc., an energy delivery company based in Calgary, Canada, and from commercially available Texas Raw Crude.

### 2.2 Mechanical Sensor/Probe

The sensor probe used for the lab test is a commercially available optical sensor for crude oil in water (Turner Designs Cyclops-7, Figure 5). The known performance of this sensor indicates it will function at depths up to 100 feet, in currents up to 0.5 knots, and perform at least five measurements per hour during a 12-hour operating window. In addition, the test team anticipates that the sensor could be mounted and deployed on a submerged ROV.



Figure 5. Turner Designs Cyclops-7 crude oil sensor.

The fluorescence oil sensor was installed into a novel fabricated probe (Figure 6). The probe holds the sensor in a fixed position to capture accurate readings while protecting it from damage. The opening in the probe was covered with a mesh screen (60 mesh/250 micron) that is porous for water and oil, but not sediment particles. This size mesh was chosen because of its availability and worked very well to filter out the sediment particles. The combined sensor/probe unit was inserted several centimeters into the laboratory oil/sediment mixtures (Figure 7) to monitor the concentration of oil in the water above and below the sediment/water interface. The sediment pore water, containing oil, diffused through the screen mesh into the interior of the probe at ambient pressure. The test team developed alternative designs that would have been used if needed, to increase flow across the sensor, e.g., active pumping and/or utilization of an optional Cyclops-7 flow-through cap (Figure 8).



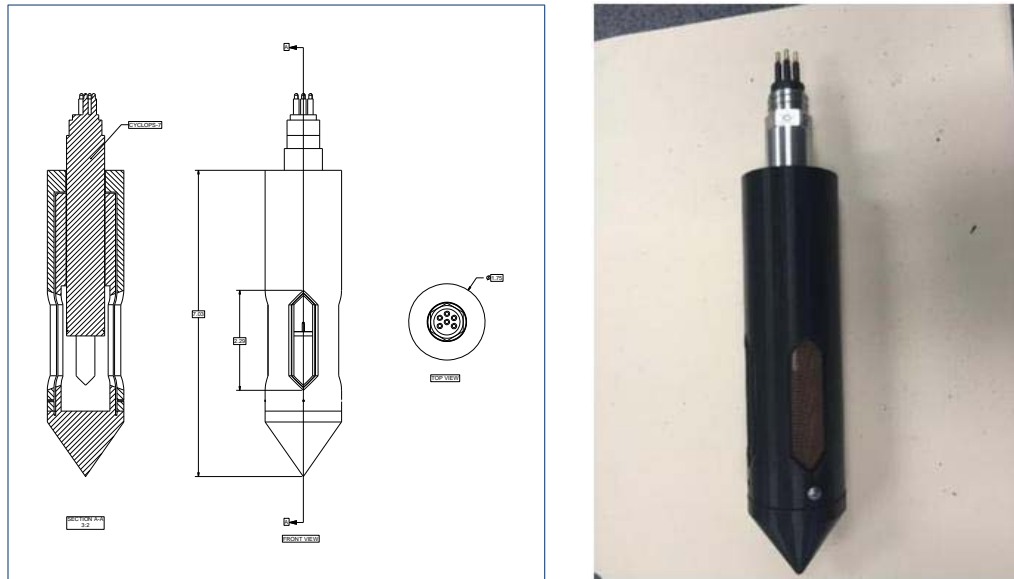


Figure 6. Prototype SOMS probe and sensor.

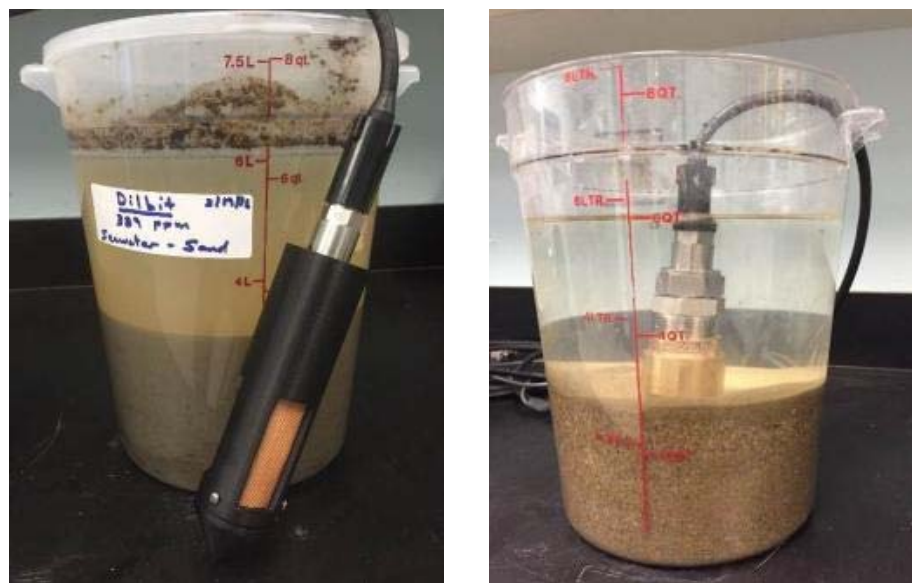


Figure 7. Prototype crude oil sensor shown housed in a probe to be inserted in oil-impacted sediments.

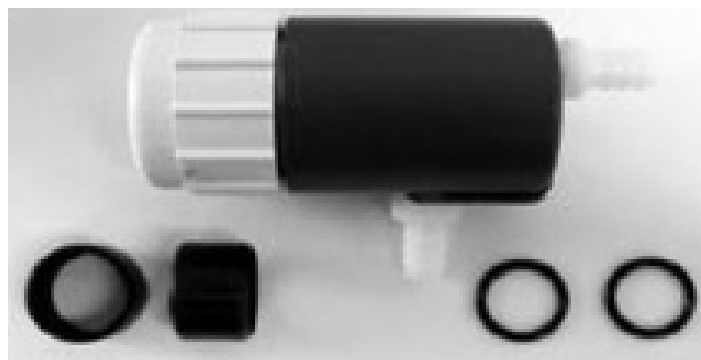


Figure 8. Optional Cyclops-7 flow through cap.

### 2.3 Data Collection

A Turner Designs Cyclops Explorer interface cable and software set was used to record the sensor readings in the lab. This interface cable provides real-time data collection of the sensor's analog output voltage over a USB connection to a Windows-based computer (Figure 9). Each data point is time-stamped and displayed as a time-series plot in the Cyclops Explorer application. The collected sensor voltage data can also be exported into comma separated value (CSV) text files, and readily exported into a Microsoft (MS) Excel spreadsheet for generating calibration calculations and graphical plots of the data. A screen shot of the data measurement during the study is shown in Figure 10.



Figure 9. Turner Designs Cyclops Explorer interface cable and software.



Figure 10. Probe measurement screen capture.

### 2.4 Step-by-Step Process

A step-by-step process was developed for the demonstration. Due to the experimental nature of the laboratory work, some of the steps were modified as progress was made and results evaluated. For example, the test team did not initially plan to use a fluorescence reference standard, as described in Step 2, but SubChem found that it improved the accuracy and stability of the Cyclops-7 sensor data. The general process is described in this section, with additional details provided in APPENDIX B.

**Step 1:** Acquire the required materials for the research.

**Step 2:** Calibrate the Cyclops-7 crude oil sensors. Since the objective is to develop a process that may work on many types of oil, two widely different crude oils (Texas Raw Crude and Dilbit) were used in this study. Therefore, sensor calibration was performed using both types of oil. In addition, a fluorescence standard (quinine sulfate) was used to improve the accuracy of the data.

**Step 3:** Characterize the particle size distribution of the dry sand using a sand mesh sieve set.

**Step 4:** Prepare a range of oil/sediment/water mixtures for both Texas Raw Crude and Dilbit. Due to the hydrophobic nature of Dilbit, preparing the sediment mixtures proved to be one of the most challenging aspects of this study.

**Step 5:** Develop a process to measure the TPH concentration of the sediment mixtures using an independent method (Dexsil PetroFlag TPH test kit). This process is very different from measuring TPH with the Cyclops-7 sensor, because the PetroFlag test is performed using a 2-10 gram sample of dry or moist sediment.

**Step 6:** Measure the TPH concentration in the sediment mixtures using the Cyclops-7 sensor in the prototype probe housing. Calculate predictive mathematical relationships between the sensor data and the TPH concentrations for both types of oil. Repeat as needed to establish repeatability.

**Step 7:** Modify the sensor probe as needed to improve performance. Several iterations are required to arrive at a “final” prototype for this study.

## 3 RESULTS

### 3.1 Testing

#### 3.1.1 Pre-Demonstration Tests

For this testing, 17 experimental containers were prepared containing equal quantities of sediment (4.5 kg), seawater (4.5 kg), and different added concentrations of either Texas Raw Crude or Dilbit oils (0-10,000 parts per million (ppm)) (Figure 3).

The first four experimental samples, prepared on 19 February included:

1. Control A: with Commercial Sand, Sargasso Seawater, with no added oil.
2. Texas Raw Crude (Target 390 ppm) added to Sargasso Seawater and Commercial Sand.
3. Dilbit Crude (Target 390 ppm) added to Sargasso Seawater and Commercial Sand.
4. Narragansett Bay: Real Beach Sand and Bay Water, with no added oil.



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Most of the second group of 13 treatments for Texas crude and Dilbit was prepared on 19 April, by first adding crude oil to the dry sand, mixing well and then adding the seawater and remixing. The two higher concentration Dilbit treatments for 5000 and 10000ppm (Treatments 12 and 13), were prepared on 25 April. These 13 treatments included:

1. Control B: with Commercial Sand, Seawater and no oil added
2. TR2 Texas Raw Crude (Target 500 ppm) added to Seawater and Commercial Sand.
3. TR3 Texas Raw Crude (Target 1000 ppm) added to Seawater and Commercial Sand.
4. TR4 Texas Raw Crude (Target 1500 ppm) added to Seawater and Commercial Sand.
5. TR5 Texas Raw Crude (Target 2000 ppm) added to Seawater and Commercial Sand.
6. TR6 Texas Raw Crude (Target 3000 ppm) added to Seawater and Commercial Sand.
7. DB7 Dilbit Crude (Target 500 ppm) added to Seawater and Commercial Sand.
8. DB8 Dilbit Crude (Target 1000 ppm) added to Seawater and Commercial Sand.
9. DB9 Dilbit Crude (Target 1500 ppm) added to Seawater and Commercial Sand.
10. DB10 Dilbit Crude (Target 2000 ppm) added to Seawater and Commercial Sand.
11. DB11 Dilbit Crude (Target 3000 ppm) added to Seawater and Commercial Sand.
12. DB12 Dilbit Crude (Target 5000 ppm) added to Seawater and Commercial Sand.
13. DB13 Dilbit Crude (Target 10,000 ppm) added to Seawater and Commercial Sand.

The following two graphs, Figure 11 and Figure 12, show the results obtained with the Prototype SOMS Probe for the Dilbit and Texas Raw Crude experimental treatments, respectively for the first 11 treatments. The two highest concentrations for dilbit (5,000 and 10,000 ppm) had results that did not correlate with the Petroflag results. It appears that these two containers may not have mixed thoroughly (see Figure D-5) so that the distribution of oil was not consistent. In addition, the thickness of the oil left on the surface did not permit a clean penetration of the surface so that the cleaner surface water filled in the void created by the sensor. These are some of the problems of this approach; a single point source of data may be insufficient in describing the oil/sediment load. The results are reported as the calculated SOMS TPH level in sediments calculated from the SOMS pore water (the water accommodated fraction or WAF) oil concentrations (Y-Axis), versus the TPH levels (X-Axis) determined in the sediments by the PetroFlag test kit on the sediments (samples collected after mixing the sediments with the seawater).



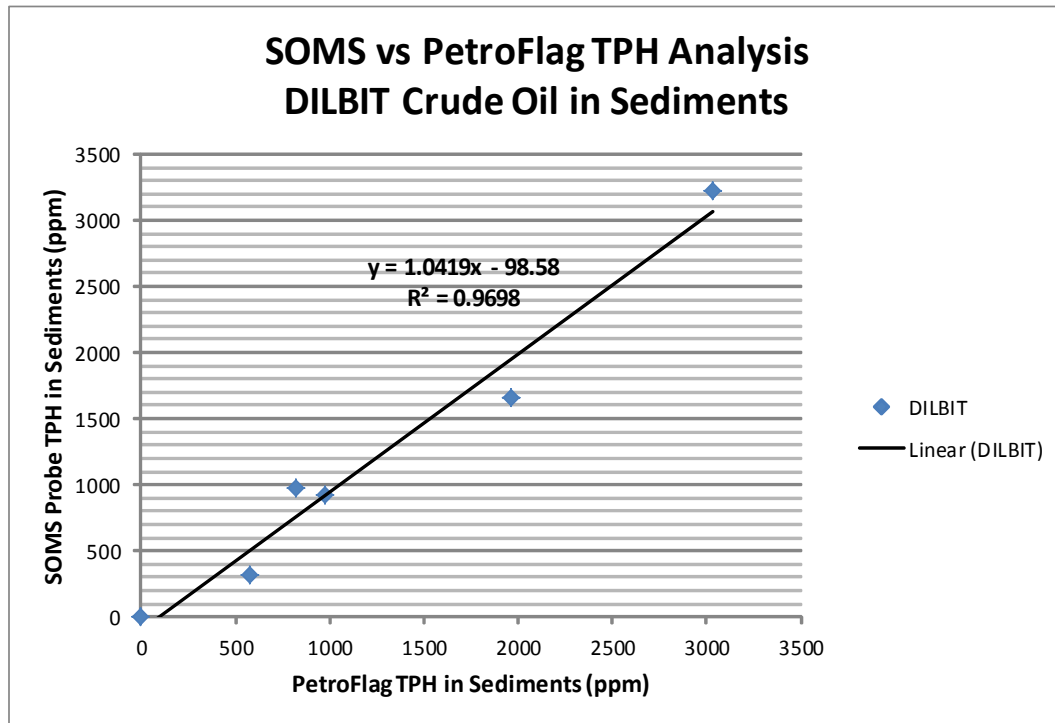


Figure 11. Results obtained with the Prototype SOMS Probe for Dilbit experimental treatments.

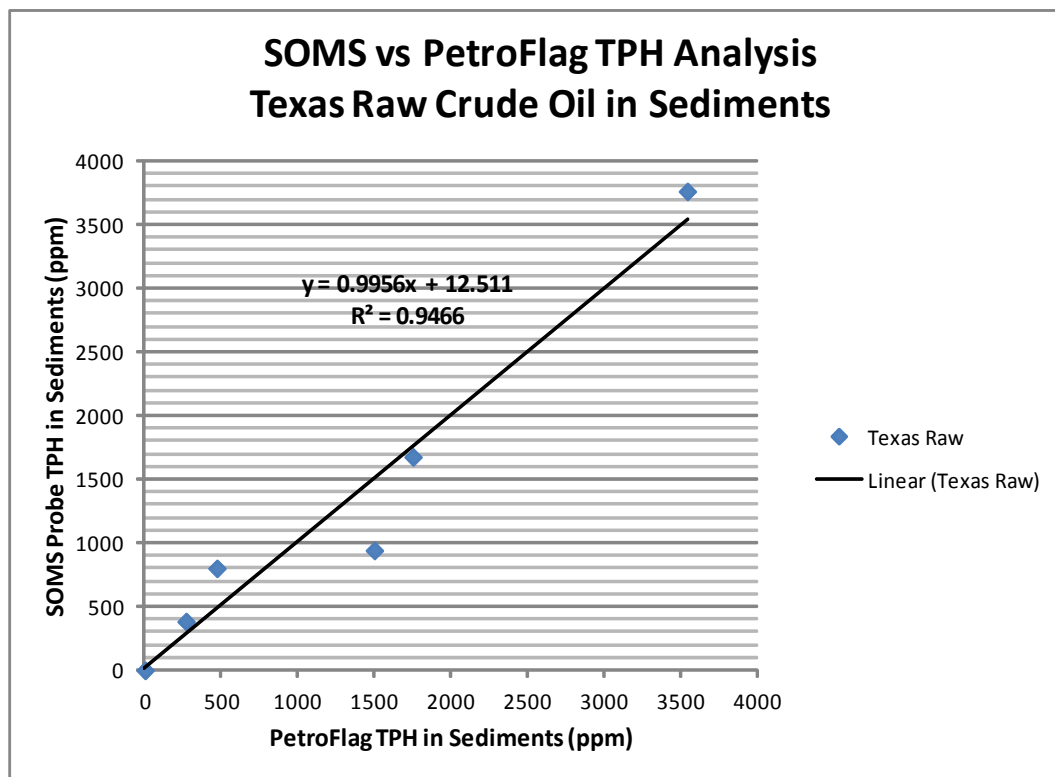


Figure 12. Results obtained with the Prototype SOMS Probe for Texas Raw Crude experimental treatments.





For all of the experimental treatments using Texas Raw Crude and Dilbit, the slopes of the regression lines, and the regression coefficients as shown in these two graphs, indicated a strong linear relationship between the concentration of oil in the sediments and the concentration of oil in the WAF of the sediment pore waters. The regression lines plot with R-Squared values over 0.94, which is good agreement. These experimental observations confirm the primary hypothesis behind the envisioned SOMS methodology, and the concentration of oil in the sediments was verifiable from both the known oil additions to the sediments, and the PetroFlag TPH analytical measurements. This linearly correlated data allowed the test team to determine the SOMS Probe oil-specific predictive relationships between the Prototype SOMS Probe measurements in sediment pore waters and the total concentration of Texas Raw Crude or Dilbit in the sediment. This indicates that the actual concentration in the sediment can be determined by measuring the probe value of the pore water and place the result into the equations below. The conclusion on the hypothesis and the accompanying predictive relationships are stated below. The pre-demonstration laboratory experiments are further detailed in APPENDIX C.

### SOMS Probe Oil-Specific Predictive Relationships:

**Texas Raw Crude: Sediment TPH (ppm) = 87.0 x (SOMS WAF Pore water, ppm) - 36 (ppm)**  
**Dilbit Crude: Sediment TPH (ppm) = 232.6 x (SOMS WAF Pore water, ppm) + 235 (ppm)**

### Confirmed Hypothesis:

*The concentration of total petroleum hydrocarbons (TPH) in crude oil impacted sediments was found to be directly related to the concentration of crude oil detected in the sediment pore waters. Applying this mathematical relationship along with the measurement of one of the two parameters, allows the prediction of the other parameter.*

#### 3.1.2 Demonstration Tests

The proof-of-concept laboratory demonstration was accomplished on 1 June at the SubChem facility, following the previously described process, to replicate the April Pre-Demonstration tests. The SOMS probe performed as expected during the demonstration, and many of the sediment mixtures produced similar results to those achieved in the April tests. Some differences were noted, however, between the prior (April) measurements and the demonstration (June) results, and this was particularly true for the higher concentration mixtures of Texas Raw Crude and Dilbit. These differences raised questions about the repeatability of the SOMS measurements and/or the stability of the experimental sediment/oil/water mixtures over time. These results for the April and June measurements are shown in Table 1, where the red entries indicate pre-demonstration (April) samples that were repeated for the demonstration.

Table 1 was created to facilitate the 1 June demonstration and records the results of the few (six) SOMS measurements made for that event. The TR 4 pre-demonstration check, made to confirm proper operation of the sensor, is included in the six results for completeness, although it was conducted on 31 May. It should be noted that a substantial quantity of data was collected both before and after the demonstration (March through June), comprising SOMS measurements (80 tests) as well as the PetroFlag measurements (55 tests). This full data set is provided in Table 3 (All PetroFlag TPH results), Table 4 (SOMS probe TPH results for mixtures prepared on 19 February), and Table 4 (SOMS probe TPH results for mixtures prepared on 21 and 25 April).



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Table 1. Comparison of six SOMS probe measurements of experimental sediments during the 1 June demonstration, with prior measurements taken on 26 April.

26 April samples repeated on 1 June are in red

| APRIL to JUNE - DEMO SOMS TESTS |           |                   |                    |               |                     |                          |                                     |
|---------------------------------|-----------|-------------------|--------------------|---------------|---------------------|--------------------------|-------------------------------------|
| Texas Raw Sample                | Date      | Expected Sediment | PetroFLAG Sediment | SOMS FL (rdg) | SOMS Calculated WAF | SOMS Calculated Sediment | SOMS April-June Relative Comparison |
|                                 |           | TPH (ppm)         | TPH (ppm)          | FL (rdg)      | TPH (ppm)           | TPH (ppm)                |                                     |
| TR 2 Sediment                   | 4/26/2016 | 509               | 443                | 1716          | 4.8                 | 383                      |                                     |
| TR 3 Sediment                   | 4/26/2016 | 1084              | 917                | 3332          | 9.6                 | 802                      |                                     |
| TR 4 Sediment                   | 4/26/2016 | 1524              | 1455               | 3874          | 11.2                | 942                      | *                                   |
| TR 5 Sediment                   | 4/26/2016 | 2025              | 1911               | 6710          | 19.7                | 1676                     | *                                   |
| TR 6 Sediment                   | 4/26/2016 | 3013              | 2954               | 14770         | 43.7                | 3763                     | *                                   |
| DEMO SOMS TESTS                 |           |                   |                    |               |                     |                          |                                     |
| TR 4 Sediment                   | 5/31/2016 | 1524              | 1455               | 3254          | 9.4                 | 782                      | 17% less                            |
| TR 5 Sediment                   | 6/1/2016  | 2025              | 1911               | 7800          | 22.9                | 1959                     | 9% more                             |
| TR 6 Sediment                   | 6/1/2016  | 3013              | 2954               | 9270          | 27.3                | 2339                     | 38% less                            |
| DILBIT Sample                   | Date      | Expected Sediment | PetroFLAG Sediment | SOMS FL (rdg) | SOMS Calculated WAF | SOMS Calculated Sediment |                                     |
|                                 |           | TPH (ppm)         | TPH (ppm)          | FL (rdg)      | TPH (ppm)           | TPH (ppm)                |                                     |
| DB 7 Sediment                   | 4/26/2016 | 493               | 441                | 160           | 0.3                 | 313                      |                                     |
| DB 8 Sediment                   | 4/26/2016 | 1016              | 999                | 555           | 3.2                 | 969                      |                                     |
| DB 9 Sediment                   | 4/26/2016 | 1522              | 1417               | 525           | 2.9                 | 920                      | *                                   |
| DB 10 Sediment                  | 4/26/2016 | 2137              | 2268               | 966           | 6.1                 | 1653                     |                                     |
| DB 11 Sediment                  | 4/26/2016 | 3018              | 3113               | 1910          | 12.8                | 3221                     | *                                   |
| DEMO SOMS TESTS                 |           |                   |                    |               |                     |                          |                                     |
| DB 9 Sediment - 1               | 6/1/2016  | 1522              | 1417               | 631           | 3.7                 | 1096                     | 19% more                            |
| DB 9 Sediment - 2               | 6/1/2016  | 1522              | 1417               | 592           | 3.4                 | 1031                     | 12% more                            |
| DB 11 Sediment                  | 6/1/2016  | 3018              | 3113               | 998           | 6.3                 | 1706                     | 47% less                            |

Table 2. PetroFlag TPH results in SOMS sediments.

| SOMs  | SOMs           | Target<br>Oil added | Estimate<br>Oil added | PETROFLAG TPH in Sediments |                           |                               |                           |
|---|----------------|---------------------|-----------------------|----------------------------|---------------------------|-------------------------------|---------------------------|
| SAMPLE No.  | SAMPLE ID      | PPM                 | PPM                   | 4/20/2016<br>PPM<br>(dry)* | 4/28/2016<br>PPM<br>(wet) | Average<br>PPM<br>(dry & wet) | 6/14/2016<br>PPM<br>(wet) |
| SOMs prepared 4/21/16 & 4/25/16   |                |                     |                       |                            |                           |                               |                           |
| 1   | Control B      | 0                   | 0                     | 1                          | 69                        | 35                            | 75                        |
| 2   | TR 2           | 500                 | 509                   | 554                        | 267                       | 411                           | 236                       |
| 3   | TR 3           | 1000                | 1084                  | 1197                       | 469                       | 833                           | 421                       |
| 4   | TR 4           | 1500                | 1524                  | 1345                       | 1497                      | 1421                          | 709                       |
| 5   | TR 5           | 2000                | 2025                  | 1960                       | 1749                      | 1855                          | 1203                      |
| 6   | TR 6           | 3000                | 3013                  | 2310                       | 3539                      | 2925                          | 1254                      |
|   |                |                     |                       |                            |                           |                               |                           |
| 7   | DB 7           | 500                 | 493                   | 255                        | 574                       | 415                           | 716                       |
| 8   | DB 8           | 1000                | 1016                  | 1164                       | 819                       | 992                           | 970                       |
| 9   | DB 9           | 1500                | 1522                  | 1750                       | 979                       | 1365                          | 1606                      |
| 10  | DB 10          | 2000                | 2137                  | 2706                       | 1960                      | 2333                          | 1778                      |
| 11  | DB 11          | 3000                | 3018                  | 3288                       | 3034                      | 3161                          | 5225                      |
| 12  | DB 12          | 5000                | 5556                  | 7531                       | 6762                      | 7147                          | 7637                      |
| 13  | DB 13          | 10000               | 11556                 | 10794                      | 11218                     | 11006                         | 17985                     |
|   |                |                     |                       |                            |                           |                               |                           |
| Older SOMs prepared 2/19/16   |                |                     |                       |                            |                           |                               |                           |
| 14  | Control A      | 0                   | 0                     | 0                          | 68                        | n/a                           | 73                        |
| 15  | Nar. Bay Beach | 0                   | 0                     | n/a                        | n/a                       | n/a                           | 37                        |
| 16  | TR 2/19        | 390                 | 373                   | n/a                        | 214                       | n/a                           | 143                       |
| 17  | DB 2/19        | 390                 | 373                   | n/a                        | 28                        | n/a                           | 400                       |
| * Dry or wet means status of weighed (2-10 gram) sediment sample as collected.        |                |                     |                       |                            |                           |                               |                           |
| A weight correction is applied based on the moisture content of wet sediment samples. |                |                     |                       |                            |                           |                               |                           |



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Table 3. SOMS Probe TPH results for mixtures prepared on 19 February.

| SOMs<br>SAMPLE No. | SOMs<br>SAMPLE ID | Estimate         | 3/24/2016      |                |                 | 4/13/2016      |                |                 | 4/26/2016      |                |                 | 6/8/2016       |                |                 |
|--------------------|-------------------|------------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|
|                    |                   | Oil added<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM |
| 14                 | Control A         | 0                | 0.0            | 0              | 0               | 0              | 0.0            | 0               | 0              | 0              | 0               | 0              | 0              | 0               |
| 15                 | Nar. Bay Beach    | 0                | n/a            | n/a            | n/a             | n/a            | n/a            | n/a             | n/a            | n/a            | n/a             | 1.6            | 1.5            | 95              |
| 16                 | TR 2/19           | 373              | 2.0            | 2.5            | 182             | 2              | 2.3            | 164             | 2.1            | 3.0            | 225             | 1.2            | 2.3            | 164             |
| 17                 | DB 2/19           | 373              | 4.0            | 3.1            | 956             | 4.3            | 0.7            | 398             | 5.6            | 1.0            | 468             | 5.2            | 2.6            | 840             |

Note: Surf. W = Surface water above sediments, Sed. PW = Sediment Porewater, Sediment = TPH estimated from SOMS PW data

Table 4. SOMS Probe TPH results for mixtures prepared on 21 and 25 April.

| SOMs<br>SAMPLE No. | SOMs<br>SAMPLE ID | Estimate         | 4/22/2016      |                |                 | 4/26/2016      |                |                 | DEMO 6/1/2016  |                |                 | 6/8/2016       |                |                 | REMIX 6/14/2016 |                |                 |
|--------------------|-------------------|------------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|-----------------|----------------|-----------------|
|                    |                   | Oil added<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM | Sed. PW<br>PPM | Sediment<br>PPM | Surf. W<br>PPM  | Sed. PW<br>PPM | Sediment<br>PPM |
| 1                  | Control B         | 0                | 0              | 0              | 0               | 0              | 0              | 0               |                |                |                 | 0              | 0              | 0               | 0               | 0              | 0               |
| 2                  | TR 2              | 509              | 1.1            | 3.9            | 303             | 1.6            | 4.8            | 382             |                |                |                 | 1.2            | 4.1            | 321             |                 |                |                 |
| 3                  | TR 3              | 1084             | 2.6            | 7.2            | 590             | 2.7            | 9.6            | 799             |                |                |                 | 2.3            | 6.9            | 564             |                 |                |                 |
| 4                  | TR 4              | 1524             | 2.3            | 10.2           | 851             | 1.2            | 11.2           | 938             | 1.7            | 9.4            | 782             | 3              | 10.4           | 869             | 2.1             | 6.9            | 564             |
| 5                  | TR 5              | 2025             | 5.8            | 16.9           | 1434            | 5.6            | 19.8           | 1687            | 2.9            | 22.9           | 1956            | 2.8            | 21.8           | 1861            | 6.6             | 22.0           | 1878            |
| 6                  | TR 6              | 3013             | 7.9            | 28.3           | 2426            | 12.2           | 43.7           | 3766            | 2.6            | 27.3           | 2339            | 7.3            | 33.4           | 2870            | 7.4             | 33.4           | 2870            |
| 7                  | DB 7              | 493              | 1.3            | 1.3            | 537             | 3.8            | 0.3            | 305             |                |                |                 | 3.3            | 2.2            | 747             |                 |                |                 |
| 8                  | DB 8              | 1016             | 2.7            | 2.5            | 817             | 3.1            | 3.2            | 979             |                |                |                 | 2.3            | 3.3            | 1003            |                 |                |                 |
| 9                  | DB 9              | 1522             | 3.8            | 2.3            | 770             | 5              | 2.9            | 910             | 7.1            | 3.5            | 1049            | 2.7            | 4.8            | 1351            | 3.9             | 4.9            | 1375            |
| 10                 | DB 10             | 2137             | 3.2            | 4.1            | 1189            | 5.1            | 6.1            | 1654            |                |                |                 | 4              | 5.4            | 1491            | 3.8             | 6.0            | 1631            |
| 11                 | DB 11             | 3018             | 3.3            | 4.2            | 1212            | 8.8            | 12.9           | 3236            | 5.8            | 6.3            | 1700            | 5.5            | 5.9            | 1607            | 5.5             | 6.6            | 1770            |
| 12                 | DB 12             | 5556             |                |                |                 | 12.8           | 5.9            | 1607            |                |                |                 | 1.3            | 2.6            | 840             |                 |                |                 |
| 13                 | DB 13             | 11556            |                |                |                 | 9.3            | 3.4            | 1026            |                |                |                 | 2.9            | 7.3            | 1933            |                 |                |                 |





### 3.1.3 Post-Demonstration Tests

To help answer questions raised during the demonstration, additional experiments were conducted to evaluate the potential variation in SOMS measurements over time, and a time-series of oil measurements on the 17 treatments using the PetroFlag and SOMS methodologies was reviewed. This section describes these additional activities. APPENDIX D further details the post-demonstration work, which concluded with a status update report and discussion of the results achieved with the RDC on 22 June.

The test team performed the following tests:

**Test 1:** Test to see if there was a systematic change in the concentration of oil detected by the SOMS Probe in the surface and/or sediment pore waters of the experimental treatments since 26 April. Used the SOMS Probe to re-measure the fluorescence of the WAF of the surface and sediment pore waters of 12 of the experimental treatments (5 Texas Raw Crude and 7 Dilbit treatments) plus two controls. These measurements were done on 8 June and compared to former values.

**Test 2:** Test to see if there was a systematic change in the TPH concentration in the sediment samples since 28 April compared to sediment core samples from 12 of the treatments (5 Texas Raw Crude and 7 Dilbit treatments) plus two controls on 14 June. Weighed out sediment samples for the analysis of TPH using the Dexsil PetroFlag Test Kits. Corrections were made for moisture content. These TPH measurements were completed on 16 June and compared to former values.

**Test 3:** Test to see if remixing the oil/sediment/water mixtures, in selected treatments, would alter the concentration of oil that would be detected by the SOMS Probe in the WAF of the surface and/or sediment pore waters of the experimental treatments. The following experimental treatments were vigorously remixed and allowed to settle for two days, before reanalysis with the SOMS probe: Control, TR4, TR5, TR6, DB9, DB10, and DB11. These seven treatments included the five treatments (Table 1) that were measured with the SOMS Probe during the demonstration on 1 June.

**Test 1 and 2 Results.** The combined results for Test 1 and Test 2 are shown for the five Texas Raw Crude (Figure 13) and seven Dilbit (Figure 14) experimental treatments. The TPH concentration detected in the sediments by the PetroFlag method in late April and early June are compared to the concentration of oil detected using the SOMS Probe in the sediment pore waters of each treatment.

For the Texas Raw Crude treatments, Figure 13 indicates that there was more oil detected by SOMS in the pore waters, relative to the PetroFlag TPH measured sediment oil contents, during early June than in late April.

For the Dilbit treatments, Figure 14 indicates that the same amount of oil was detected by SOMS in the pore waters, relative to the PetroFlag TPH measured sediment oil contents, between the early June and late April measurements. The two high Dilbit concentration samples have low results in both April and June (Table 4) as mentioned previously; but are included in the plot for completeness.



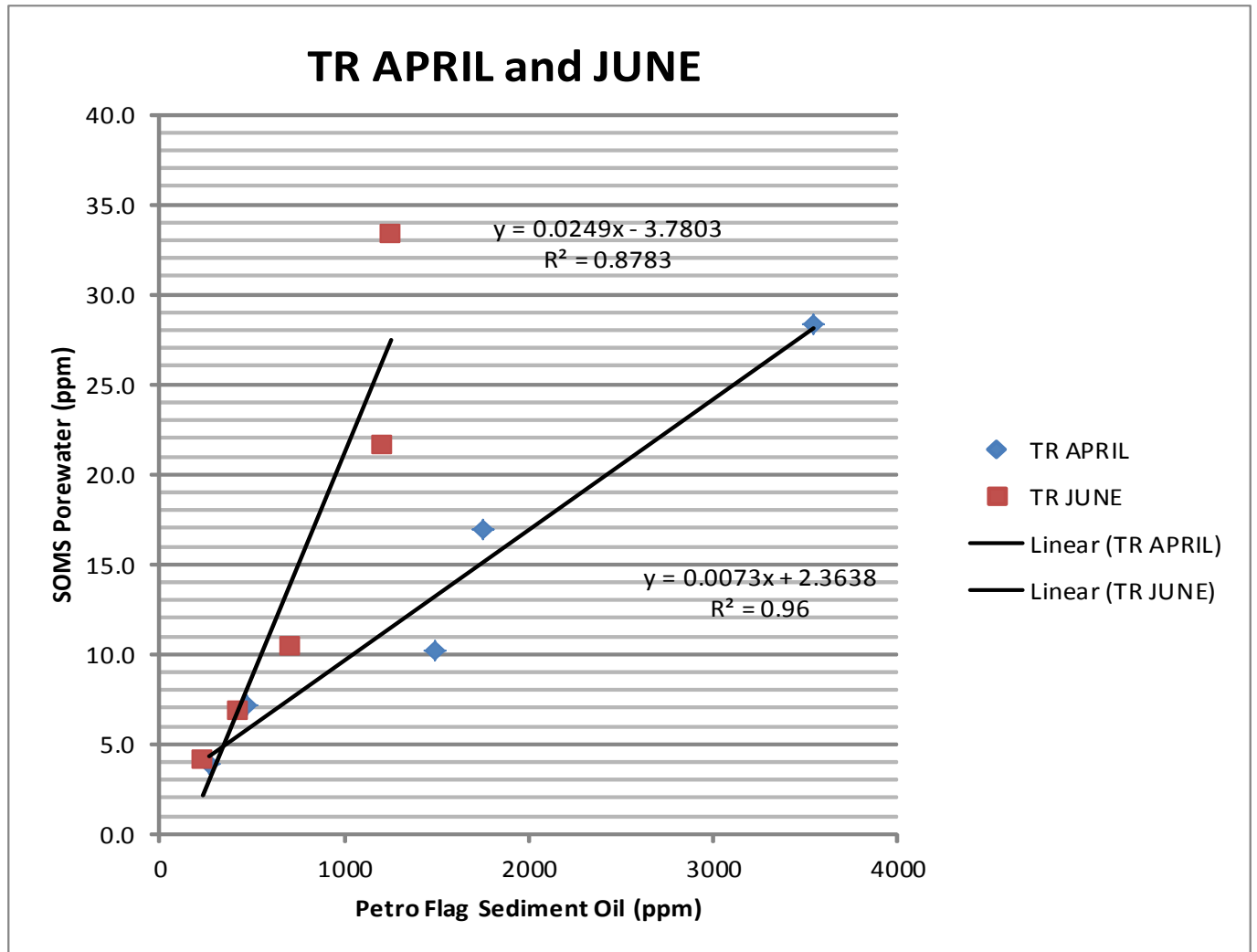


Figure 13. Combined Test 1 and 2 results for five Texas Raw Crude treatments. Comparison of late April and June SOMS Probe and PetroFlag measurements of oil in sediments and sediment pore water.

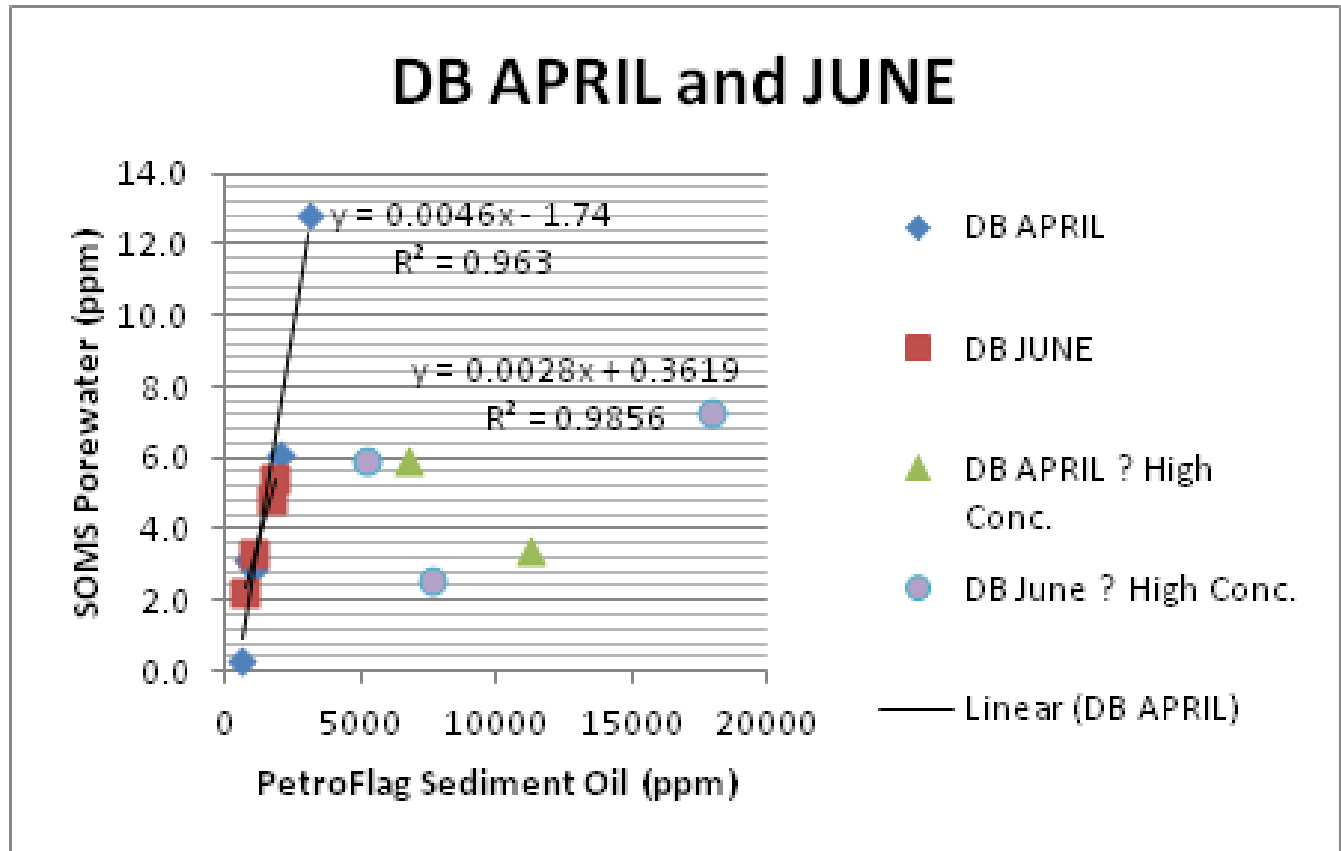


Figure 14. Combined Test 1 and 2 results for seven Dilbit Crude Oil treatments. Comparison of late April and June SOMS Probe and PetroFlag measurements of oil in sediment pore water and sediments. Note the April and June high Dilbit concentrations samples with anomalous low results (plotted separately).

**Test 3 Results.** The comparative June SOMS Probe measurements of the sediment pore water oil contents before and after remixing seven of the experimental treatments (Figure 15 and Figure 16), were surprisingly similar. This was particularly true of the 8 June (before remixing) and 14 June (after remixing) measurements. The results from the SOMS Probe measurements obtained during the 1 June demonstration are also included in the two graphs, and agree fairly well with the post-remixing SOMS Probe readings.



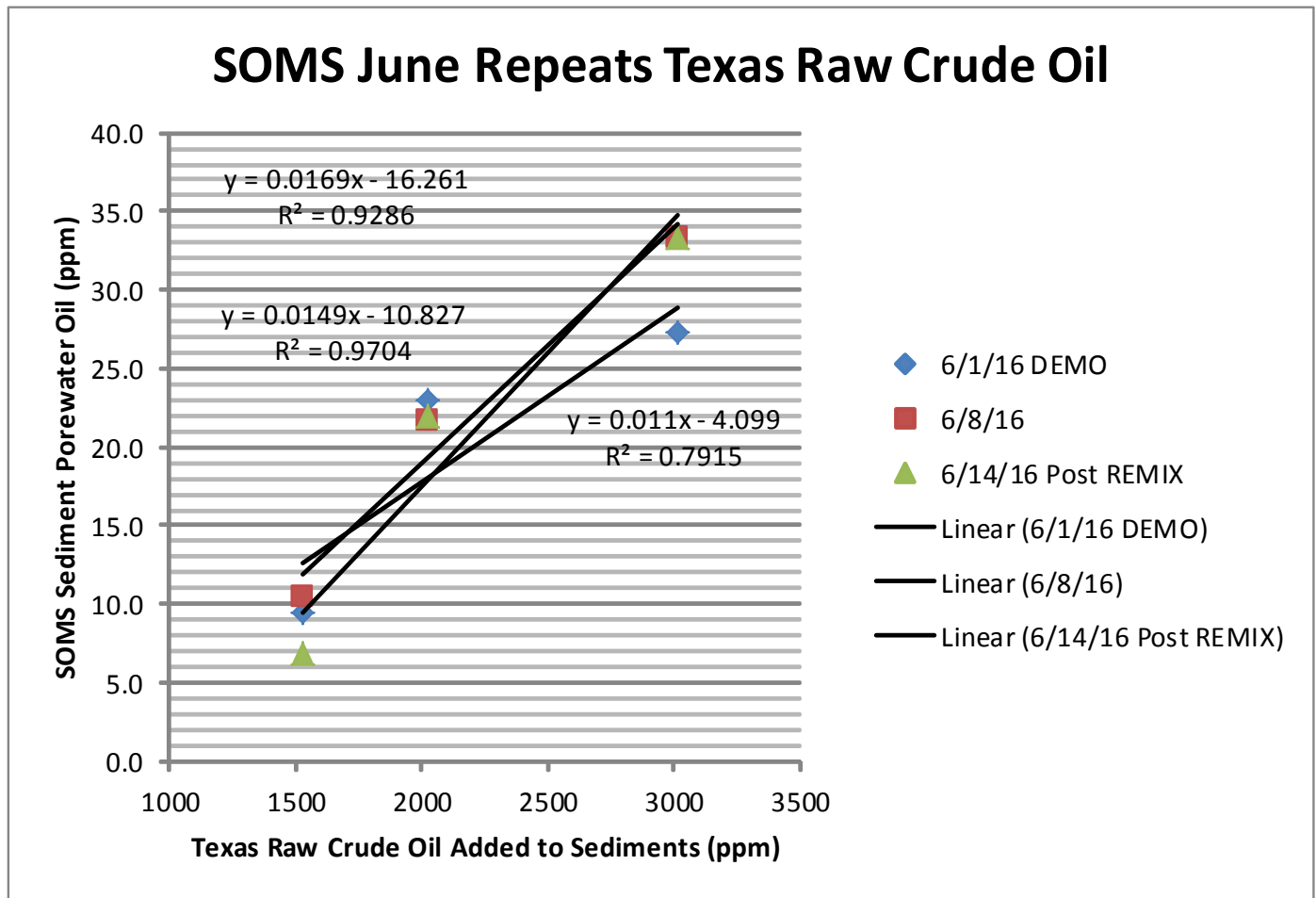


Figure 15. Test 3, Comparison of 1 and 8 June (before remix), and 14 June (post remix) SOMS measurements of Texas Raw Crude in sediment pore waters as a function of the concentration of crude oil added.

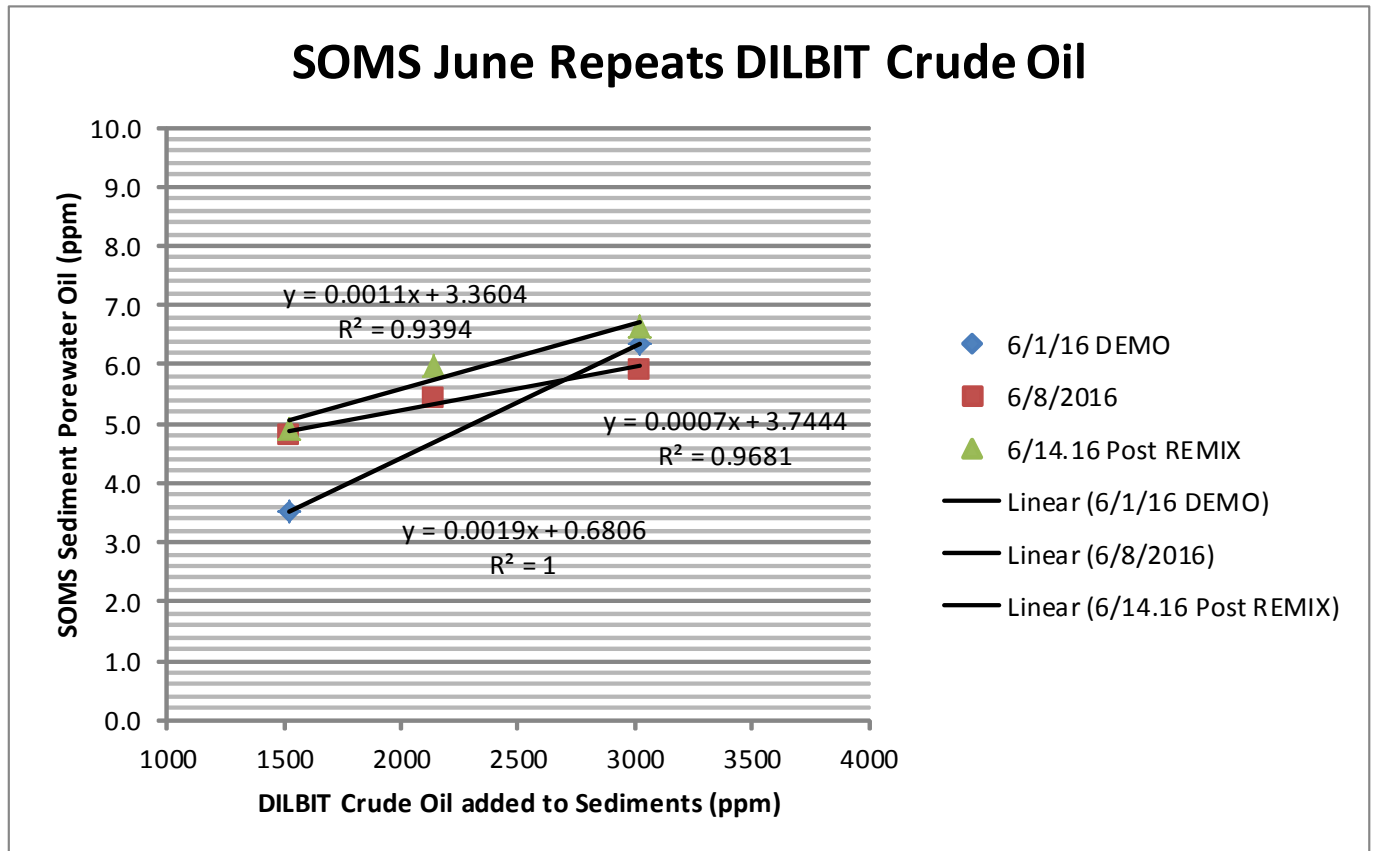


Figure 16. Test 3, Comparison of 1 and 8 June (before remix), and 14 June (post remix) SOMS measurements of Dilbit in sediment pore waters as a function of the concentration of crude oil added.

**Time Series of Oil Measurements Results.** Table 5 shows the time-series of sample preparations, PetroFlag sampling, SOMS Probe measurements and other operations involving potential disturbance of the sediments and changes to oil concentrations. After the containers were mixed and allowed to settle for two days, the SOMS Probe was used to take measurements of the oil content of the surface water and the sediment pore waters. Representative core samples were also taken (2-10 gram subsamples) to measure the sediment oil contents using the PetroFlag test kit. Seventeen experimental treatments were prepared, four on 19 February and 13 on 19 April. Since they were initially created, the water, sediment-water interface and sediments of these experimental containers were disturbed by being sampled a number of times as listed in Table 5 either to obtain a PetroFlag core sample, or to make an in situ measurement with the SOMS probe. It seems likely that the sediment penetrating PetroFlag core sampling and SOMS Probe measurements would also allow some exchange, concentration, and or dilution of oil chemical constituents between the sediments, sediment pore waters and surface waters.

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Table 5. Time-series of sample preparations, PetroFlag sampling, SOMS Probe measurements and other operations involving potential disturbance of the sediments.

| SOMS Experimental Treatments Sediment Disturbance Timeline |  |                    |           |  |
|--|--|--------------------|-----------|--|
| DATE   | Operation  | Sediment Disturbed | # Samples | Experimental Treatments                              |
| 2/19/2016  | Expt Container Prep & Mix                          | yes                | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |
| 3/24/2016  | SOMS Probe - Initial Sediment Test                 | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/13/2016  | SOMS Probe - FL of surface & sed. pore waters      | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/13/2016  | PetroFlag Core Samples- Extract and Analyze        | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/19/2016  | Expt Container Prep & Mix - No H <sub>2</sub> O    | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/20/2016  | PetroFlag Core Sample (Dry Sediment)               | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/21/2016  | Expt Container Prep & Mix - Added H <sub>2</sub> O | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/22/2016  | Cyclops 7 to measure FL of filtered supernatants   | no                 | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/22/2016  | SOMS Probe - FL of surface water                   | no                 | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/22/2016  | SOMS Probe - FL of surface & sed. pore waters      | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/25/2016  | Expt Container Prep & Mix - Added H <sub>2</sub> O | yes                | 2         | DB 12&13, ~5000 & ~ 10,000 ppm oil                   |
| 4/26/2016  | SOMS Probe - FL of surface & sed. pore waters      | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 4/26/2016  | SOMS Probe - FL of surface & sed. pore waters      | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/28/2016  | PetroFlag Core Sample (Wet Sediment)               | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 5/2/2016   | Analyze PetroFlag from 4/28/16                     | no                 | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 5/31/2016  | SOMS Probe - FL of surface & sed. Pore waters      | yes                | 1         | Pre-Demo recheck TR 4 ~1500 ppm oil                  |
| 6/1/2016   | SOMS Probe - FL of surface & sed. Pore waters      | yes                | 4         | USCG DEMO: TR 5, TR 6, DB 9, DB 11                   |
| 6/8/2016   | SOMS Probe - FL of surface & sed. Pore waters      | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 6/8/2016   | SOMS Probe - FL of surface & sed. Pore waters      | yes                | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |
| 6/14/2016  | PetroFlag Core Sample (Wet Sediment)               | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 6/14/2016  | PetroFlag Core Sample (Wet Sediment)               | yes                | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |
| 6/14/2016  | Expt Container Re-Mix                              | yes                | 7         | Control B, TR 4,5,6, DB 9,10,11 ~1500 - 3000 ppm oil |
| 6/16/2016  | SOMS Probe - FL of surface & sed. Pore waters      | yes                | 7         | Control B, TR 4,5,6, DB 9,10,11 ~1500 - 3000 ppm oil |
| 6/16/2016  | Analyze PetroFlag from 6/14/16                     | no                 | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 6/16/2016  | Analyze PetroFlag from 6/14/16                     | no                 | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |

The concentration of crude oil in the sediments was experimentally defined by two methods:

1. Precisely knowing the weight of crude oil added to the sediment and
2. Precisely measuring the concentration of total petroleum hydrocarbons (TPH) in a sediment sample using the Dexsil PetroFlag TPH test kit.

The crude oil (a complex mixture of organic chemicals) was homogeneously mixed/blended to prepare the experimental treatments. During (and after) these mixing events, the crude oil components had an opportunity to end up where they preferred to be, based upon their physiochemical properties (i.e. solubility, hydrophobic or hydrophilic nature, viscosity, volatility, etc.). There are seven potential locations (or variables) for the crude oil organic chemical components:

1. In the sediments (adsorbed, as various sized oil/tar-like droplets and/or oil-sand agglomerates),
2. dissolved or suspended as droplets in the sediment pore waters,
3. at the sediment-water interface,
4. dissolved or suspended as droplets in the surface water layer,
5. absorbed to the container walls,
6. at the air-water interface, and
7. in the atmosphere.

The aggressive mixing imparted energy to the oil/sediment/water mixtures, and essentially set up a multi-phase system that was not in physio-chemical equilibrium. After the mixing stopped, and the containers sat on the bench for two to four months, the chemical components of the oil were free to weather, diffuse and migrate at some rate, towards a more equilibrated state.

**Overall Results.** Based on the theoretical considerations, the pre-demonstration laboratory experiments described above and detailed in APPENDIX C, the post-demonstration experiments described above and detailed in APPENDIX D, and a review of the experimental time series data resulting from that effort, the test team concluded:

1. The SOMS probe technique worked as expected for measuring the relative concentration of crude oil in the sediments contained in the experimental treatments.
2. There were changes observed over time in the SOMS and PetroFlag results for measurements of crude oil in the 17 experimental containers.
3. The two types of crude oil had different temporal responses.
4. The observed differences in the SOMS and PetroFlag measurement of oil concentrations over time are largely attributable to actual changes in the crude oil distribution or concentration that occurred in the sediment, water and air phases of the laboratory experimental containers.
5. The hypothesis and mathematical relationships described earlier remain valid for the measurement of oil in underwater sediments, based on testing using Texas Raw Crude and Dilbit.

### 3.2 Texas Raw Crude vs. Dilbit Observations

Several differences were noted between these two types of crude oil during the study.

- Dilbit is significantly more difficult to use in preparing oil/sediment/water mixtures. This is largely due to its hydrophobic nature; its propensity to adhere to all surfaces, including plastic, Teflon, and glass - materials commonly used to contain and mix the sediments in the laboratory. A much larger proportion of Dilbit adhered to such materials than did the Texas Raw Crude. The test team believes the same difficulty would be experienced with other Dilbits, however, since Dilbit formulations vary and the added components are proprietary, it is not certain how broadly this experience can be extrapolated.
- Dilbit appeared to be less stable in the oil/sediment/water mixtures, particularly in higher concentrations over time, the Dilbit appeared in cross section as a fine line at the sediment-water, and water-air interfaces of the mixtures, and interspersed as surface spotting (mini-tarballs) as viewed from above the containers (Figure 17).
- Dilbit was relatively noxious compared to the Texas Raw Crude when working with both in the lab. Over a short time however, the lighter Dilbit chemical components appeared to dissipate significantly.

### 3.3 Findings

The conceptual system developed in this project may be useful in limited conditions. The prototype appears to detect oil if the concentrations are low and oil exists in the interstitial locations between the sand grains. This was confirmed by the high correlation values for the straight lines in all of the graphs for both the confirmation of the calculations using the PetroFlag as well as the concentration values. Results were inconclusive if the prototype is useful for higher concentrations or with higher viscosity oil that readily





sticks to the grains of sand and silt. Many of the higher concentrations had values outside the expected values as given by the straight lines. The process for evaluation using the smaller samples for the bench-top system may also be inadequate, as the mixing process does not replicate the actual processes that occur in the field. A major drawback is that the procedure also needs to be repeated and recalibrated for each type of oil and condition.



Figure 17. Example of mini-tarballs forming on the mixture surface after two months.

## 4 RECOMMENDATIONS

This was only a preliminary attempt to develop a system that can easily sample the bottom of a body of water quickly and efficiently. There are other sensors and processes on the market that potentially could be adapted for this use. This section presents recommendations (Table 6, Table 7, and Table 8) for adapting fluorometry technology and process, that was demonstrated with the bench top system, to a notional system that could be mounted on an ROV for field-testing (notional schematic shown in Figure 18 ). The concept of operations (CONOP) outlined below provides a context for testing the envisioned working system. Attributes for a potentially suitable ROV are provided in APPENDIX E that could be used for other sensors as well.



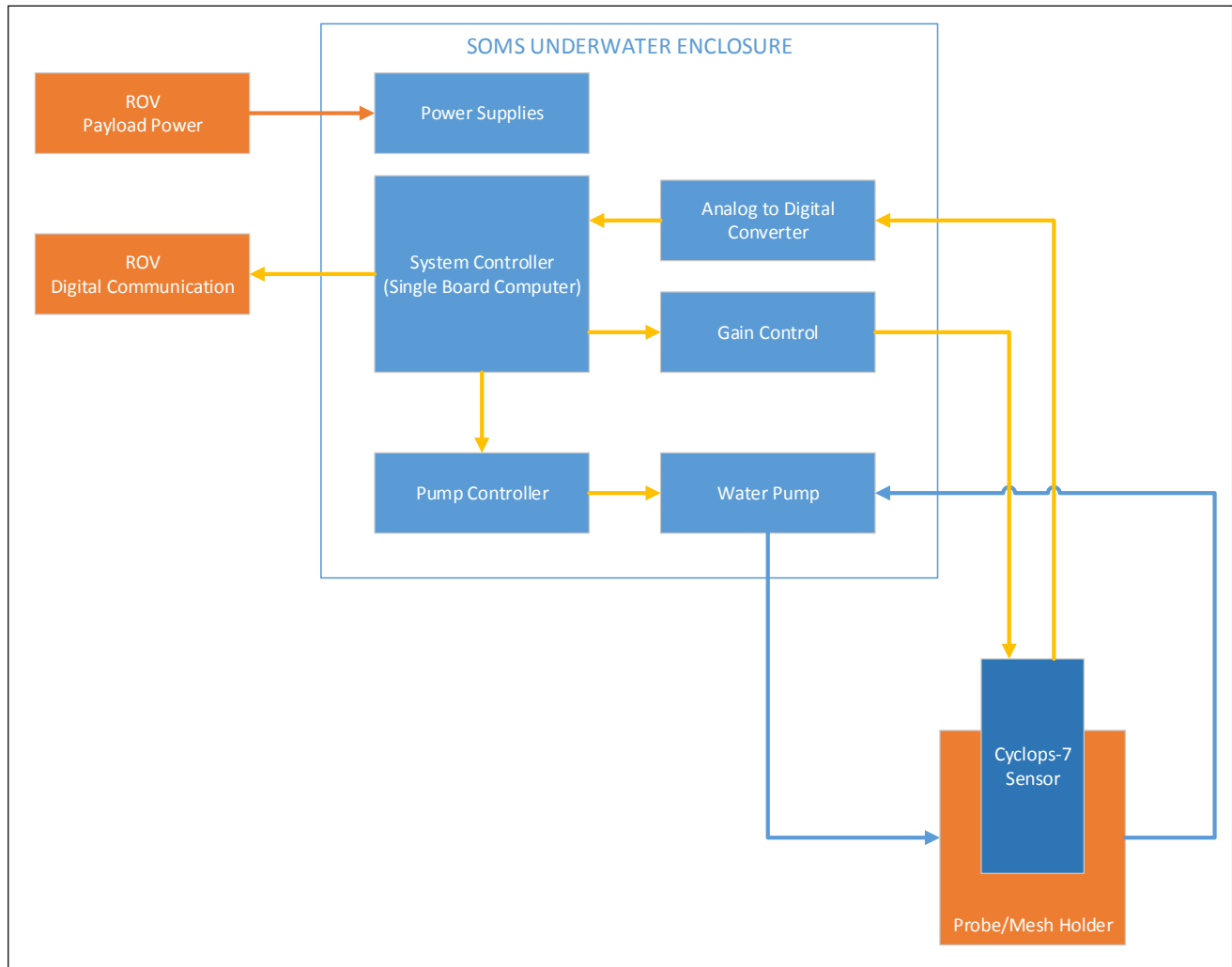


Figure 18. Notional schematic for SOMS field system.

### 4.1 SOMS NOTIONAL CONOP

A response asset operated by the USCG, another Government agency or a contractor will lower into the water, a ROV that has been selected to optimize the mission, and take sediment measurements. The ROV will be a commercial item that may require modifications to mount the SOMS and integrate, as much as practicable, common requirements, such as power, control, and data transmission. Ultimately, the ROV may carry attached systems in a more integrated, industry standard manner.

The current effort, however, is to attach the SOMS to a ROV sufficient to transport the SOMS to the desired environment to conduct testing. To simplify the effort and support this future testing phase, the SOMS will operate independently of the ROV, i.e., separate cables, power, etc. This is necessary because variation in ROV design leaves many essential details unknown (e.g., electromechanical control cable vs. optical control cable), and the huge cost and effort that would be required to develop an integrated system does not further the test objectives, which is to assess a SOMS in the field. On the other hand, some ROV attributes that are important to successful SOMS operation, in particular stability and mobility on the bottom sediment, are required to accomplish the test objectives.

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The SOMS will function at depths of up to 100 feet, in currents of up to 0.5 knots, and collect at least five (5) samples per hour during a 12-hour operating window without bringing a sample to the surface. Operations may take place day or night, during inclement weather, and in a range of air temperatures to be determined by the RDC. Sea state is limited by the capability of the platform used and personnel safety concerns rather than the SOMS and ROV. The ROV will not be man-portable but will require weight-handling gear to deploy and retrieve. The SOMS and ROV will be controlled onboard the deployment platform. The area where the SOMS is deployed may contain oil in the water column or on the bottom.

### 4.2 Sensor/Probe

Table 6. Sensor / probe recommended attributes.

| Area                                     | Recommendation   |
|--|--|
| Probe durability                         | The original laboratory test probe was made of Acrylon Butadiene Styrene (ABS) plastic, with a hollow internal shell, and failed during laboratory testing. A replacement probe using a solid shell of nylon material performed well in laboratory testing. To maximize durability, use a non-corrosive metal, e.g., bronze for the impact point to withstand long-term wear from sediment and impact from aggregate in the bottom sediment. Use modular components that can provide the ability to replace sections that are more susceptible to damage, e.g., impact point or mesh screen. |
| Probe shape                              | The current probe may not be the most effective shape. Design the probe end as a removable component so candidate designs may be easily changed and evaluated.   |
| Probe insertion                          | Provide a mechanism to insert the probe into the sediment. Laboratory testing has shown that a twisting motion facilitates insertion and may be required to insert past aggregate in the sediment. Other approaches such as vibration may also be worth considering.   |
| Probe depth                              | If the probe insertion depth is not tightly controlled, the data may be inconsistent, resulting in a poor characterization of TPH in the sediment. Include a depth gage for probe insertion, which will generate data to correlate with TPH and location. Deploy SOMS on a ROV with adequate downward force to support the probe insertion procedure. This may be achieved by weight or vertical thrusting force.  |
| Mesh screen                              | An easily removable mesh screen was used during bench top testing to ensure a proper screen size. The screen was held in place by set screws to facilitate changing sizes. Recommend a more permanent mounting, e.g., fuse the appropriate size mesh screen to a metal housing, or if different sizes are needed, design as a probe component that can be easily swapped out.  |
| Mesh screen                              | The mesh screen could be damaged by repeated insertion into sediment of unknown composition. Consider a modified design for the probe that would enter the sediment and pass the sample water through a tube to a mesh screen and sensor located away from the probe insertion area.   |
| Sample water flow                        | A fine mesh keeps out sediment but slows water flow through the sensing chamber. This concern increases if the sensor is located further away from the probe. If needed, use an alternative design, e.g., a pump to draw water from the probe through the tube to the sensor, or a flow through cap (option provided for the Cyclops-7 sensor).  |
| Clearing fouled screen                   | Fouling the screen with sediment is possible, as sample water is pumped through the sensor chamber. A method is needed to detect this condition and to remove this sediment (e.g., backflush) from the screen while the SOMS remains underwater at depth.  |
| Protection from damage and contamination | In some cases, there may be oil present in the water column or on the bottom. A device will be needed to prevent the Cyclops-7 sensor from being contaminated by this oil. In addition, the mesh screen is relatively vulnerable and may need physical protection from damage. A retractable sleeve could be used to prevent contamination as well as protect from damage. This could be opened and closed through a spring-loaded design.   |
| Process                                  | A specific process is needed for operational use to include calibration to obtain the best quality data that can be useful in various environmental conditions and oil types.  |



### 4.3 Data Acquisition and Control Systems

Table 7. Data acquisition and control systems recommended attributes.

| Area  | Recommendation   |
|---|--|
| Enclosure                                     | Individual SOMS components cannot practically be mounted individually on a ROV. Components should be integrated in a mountable enclosure that simplifies mounting on the ROV, minimizes snagging, and provides protection for the components and connections.  |
| Watertight connections                        | All underwater electronics connections must be watertight to 100 feet with a built-in safety margin.   |
| Probe electronics                             | Probe gain control (two selection switches between probe wires and ground)<br>Water pump control electronics.<br>Analog-to-digital converter (ADC) to sample probe voltage.  |
| Control software                              | Single board computer (SBC) to read ADC and provide sample info to ROV.<br>Interface between water pump control and SBC.<br>Software on SBC to control events and timing between water pump, probe sampling, gain level, communication to ROV, etc.<br>In the event of any software issues, technicians need access to the control software to resolve problems, and allow the measurement to continue. Provide additional connector for system programming and debug.<br>Method to reset system in case of SBC software issue.<br>Need to detect when a sample is read by the probe, but probe was not properly inserted in sediment (refer to Probe depth in Table 6). |
| Items for a future, fully integrated SOMS/ROV | Software on ROV to accept sample information and to pass along control commands from the surface.<br>Software on surface ROV control laptop to allow user to start sampling, check for errors, record samples to file.<br>Data collection may be enhanced by adding the capability to take photos and record voice notes that can be correlated as TPH measurements are taken.   |

### 4.4 Procedures

Table 8. Procedural recommendations.

| Area              | Recommendation   |
|-------------------|--|
| Sampling approach | Current and disturbed sediment due to probe insertion may influence where samples are taken. In addition, the bottom sediment may not be homogenous over the bottom area. Develop sampling tactics that recognize these factors. For example, if current is present, sample heading into the current to avoid disturbed sediment flowing into a subsequent insertion area. For example, take a matrix of samples over a small area to help characterize the TPH content. |

### 4.5 Shallow Water SOMS

In addition to the above recommendations, which focus on a SOMS that would meet the operational requirements established by the RDC (e.g., 100 foot depth), a potentially useful variant would be a SOMS designed for use in very shallow water, i.e. 10 foot water depth. The primary disadvantages of such a system are the depth limitation, and the dependence on good surface weather conditions. The advantages of such a system, however, are:

- Easy to transport and deploy (no weight handling system required).
- Flexibility in deployment location (off of a boat, pier, oil platform).



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- Less expensive (no ROV, related control systems or camera).
- Less complex (shorter connections, positioning is done manually vice a powered system, probe rotation is accomplished by hand instead of electro-mechanical means).
- Data acquisition system and power supply requirements are minimal (similar to the laboratory setup).
- Positive control over probe insertion depth, with some tactile feedback.
- May be useful in high current environments, where controlling an ROV would be problematic.
- Some flexibility in capability, i.e., simple pole and connection extensions may marginally increase depth.
- In some locations, the bottom may be visible at the surface, aiding the operator in setting sample locations.
- Faster and easier to retrieve in the event of failure or negative data indications.

Designing a shallow water system could be as simple as extending the data and power connections of the laboratory system, attaching the probe on one end, and securing the components (probe and cables) on the pole. The pole could be one-piece or locking sections. A simple setup could be made, for example, from 2" Schedule 80 PVC pipe, with a T-handle at the top for rotating the pole. The wire connections could be cable-tied externally or run inside the pole, and the probe could be held in position by screws, cable ties or other means. A positive stop at the bottom of the pole would be needed to insert the probe to a uniform depth. The probe used in the current study is configured to penetrate only 5 inches into the sediment, in which case, the depth stop would be located partway up the probe body. A different probe, or other depth stop configurations could allow the probe to be inserted further into the sediment. The depth stop may be attached to the probe itself or to the pole. The depth stop could be as simple as a T-handle or disk attached near the bottom of the pole, but must allow the pole to rotate to aid insertion. As noted for the SOMS field system above, a retractable sleeve could be included to protect the screen and sensor from damage, and prevent contamination of the Cyclops-7 sensor when inserting the probe through a layer of oil in the water column or on the bottom.

Figure 19 shows a notional shallow water system, based on an augmented laboratory setup.

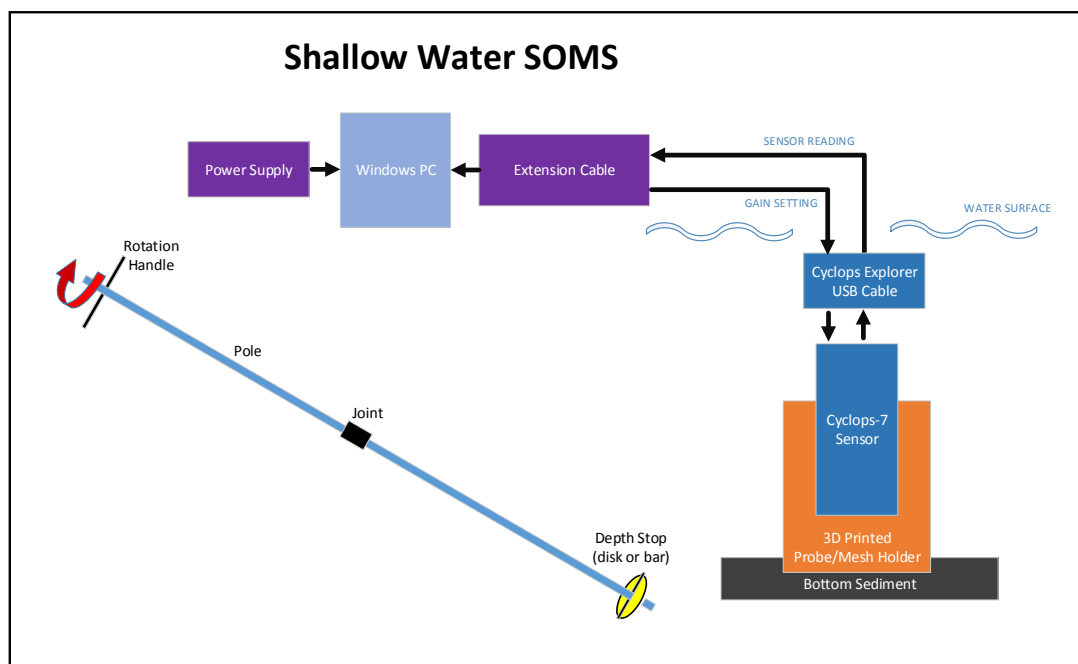


Figure 19. Notional schematic for SOMS shallow water system.



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### APPENDIX A. COMPARISON OF PHYSICAL PROPERTIES OF CRUDE OILS

The current research focused on two different crude oil samples, 1) a sample of Dilbit crude oil obtained from the Enbridge Pipeline ([www.enbridge.com](http://www.enbridge.com)) and 2) Texas Raw crude, a representative light crude oil, available commercially from Texas Raw Crude International (<http://www.texasrawcrude.com/>), which provides samples of light crude oil for research and educational purposes. Unfortunately, the Enbridge Dilbit crude oil sample did not come with any specific information about its proprietary composition or physical properties. The general properties of Dilbit, however, are shown in Table A-1, and can be compared to the general properties of light crude oil, also shown in the table.

Table A-1. Range of physical properties for example oil types.

| Property            | Units                     | Oil Types |           |             |   |              |                       |                  |                    |
|---------------------|---------------------------|-----------|-----------|-------------|---|--------------|-----------------------|------------------|--------------------|
|                     |                           | Gasoline  | Diesel    | Light Crude | Dilbit <sup>1</sup>                     | Heavy Crude  | Intermediate Fuel Oil | Bunker C         | Crude Oil Emulsion |
| Density             | Kg/m <sup>3</sup> at 15°C | 720       | 840       | 780 to 880  | 824 to 941                              | 880 to 1000  | 940 to 990            | 960 to 1040      | 950 to 1000        |
| API Gravity         |                           | 65        | 35        | 30 to 50    | 18 to 39                                | 10 to 30     | 10 to 20              | 5 to 15          | 10 to 15           |
| Viscosity           | mPas at 15°C              | 0.5       | 2         | 5 to 50     | 270.5* to 265,263**                     | 50 to 50,000 | 1,000 to 15,000       | 10,000 to 50,000 | 20,000 to 100,000  |
| Flash point         | 15°C                      | -35       | 45        | -30 to 30   | <-35** <sup>m</sup> to 58* <sup>m</sup> | -30 to 60    | 80 to 100             | >100             | >80                |
| Solubility in Water | ppm                       | 200       | 40        | 10 to 50    | -                                       | 5 to 30      | 10 to 30              | 1 to 5           | -                  |
| Pour Point          | °C                        | NR        | -35 TO -1 | -40 to 30   | -30* <sup>m</sup> to 15* <sup>m</sup>   | -40 to 30    | -10 to 10             | 5 to 20          | >50                |
| Interfacial Tension | mN/m at 15°C              | 27        | 27        | 10 to 30    | 27* <sup>m</sup> to 150* <sup>m</sup>   | 15 to 30     | 25 to 30              | 25 to 35         | -                  |

Modified from Fingas (2001); <sup>1</sup>Values provided include weathered dilbit from tests; NA= not relevant; \* Calculated for AWB; \*\* Calculated value for CL; \*<sup>m</sup> Measured value of AWB; \*\*<sup>m</sup> Measured value of CL

The Texas Raw crude used in this research was West Texas Intermediate (WTI) crude oil, also known as Texas Sweet Light, the highest grade crude oil traded on the New York Mercantile Exchange. It is the base, to which all other crude oils are compared. The oil that Texas Raw Crude provides is in its most natural state; unrefined and directly from the well.

Crude Oil has three main physical properties: density, viscosity, and solubility (Polaris Applied Sciences Inc. (2013). Typical physical properties for a broad range of oil types are summarized above in the table and at [https://crrc.unh.edu/sites/crrc.unh.edu/files/comparison\\_bitumen\\_other\\_oils\\_polaris\\_2014.pdf](https://crrc.unh.edu/sites/crrc.unh.edu/files/comparison_bitumen_other_oils_polaris_2014.pdf).

Characteristics such as color, gravity, small amounts of water, etc. may vary. WTI is a light crude oil, with an American Petroleum Institute (API) gravity of around 39.6 and specific gravity of about 0.827. The kinematic *viscosity* is 4.9 [mm<sup>2</sup>/s] at 20 °C and the aqueous solubility is ~ 28 mg/L. It contains about 0.24% sulfur, and is rated as a sweet crude oil (having less than 0.5% sulfur). WTI is refined mostly in the Midwest and Gulf Coast regions in the U.S., since it is high quality fuel and is produced within this country.





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### APPENDIX B. STEP-BY-STEP PROCESS

The below steps are prescribed to construct a bench-top SOMS.

1. Acquire the needed materials and equipment for the research. The primary materials and equipment needed for this research include:
  - Samples of crude oils (Dilbit and Texas Raw Crude),
  - Fine-grained sand and natural marine sediment,
  - Coastal, and ocean seawater,
  - Cyclops-7<sup>®</sup> crude oil sensors,
  - Explorer<sup>®</sup> power and data interface,
  - Dexsil PetroFlag<sup>®</sup> TPH test kit,
  - Plastic experimental containers,
  - An oil/sediment/water mixing device (Figure B-1),
  - A sieve mesh screen set for characterizing sediment-grain size distributions (Figure B-1),
  - A custom fabricated (SAIC-designed) probe housing for the sensor and mesh screen.

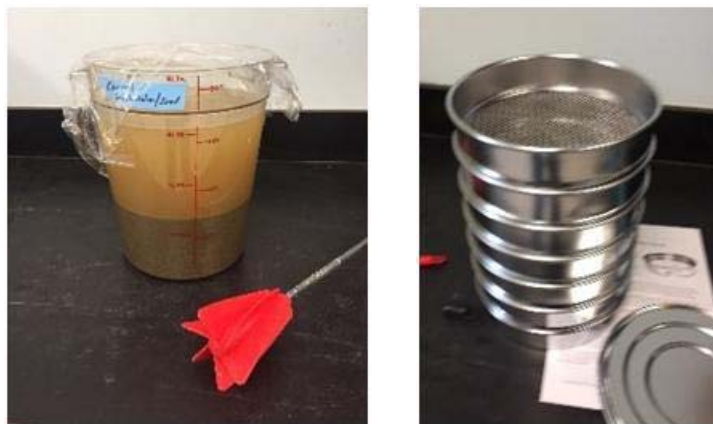


Figure B-1. Oil/sediment/water mixing device (left) and sieve mesh screen set (right).

2. Evaluate and calibrate the Cyclops-7 crude oil sensors (Figure B-2) using a prepared series of standards in seawater with different concentrations in two types of crude oil: Texas Raw Crude and Dilbit. Prepare a series of Quinine Sulfate standards to use as stable comparative fluorescence reference standards (Figure B-3, Figure B-4). Quinine sulfate, dissolved in dilute acidic media, is a polycyclic aromatic hydrocarbon (PAH) that has been widely used as a standard for static fluorescence measurements. These evaluations and calibrations should be performed with and without the Cyclops-7 sensor prototype probe housing. The calibration data (oil concentrations versus fluorescence readings) are used to calculate the concentrations in the known and unknown sediment samples tested (see step 4 for sample calculation).

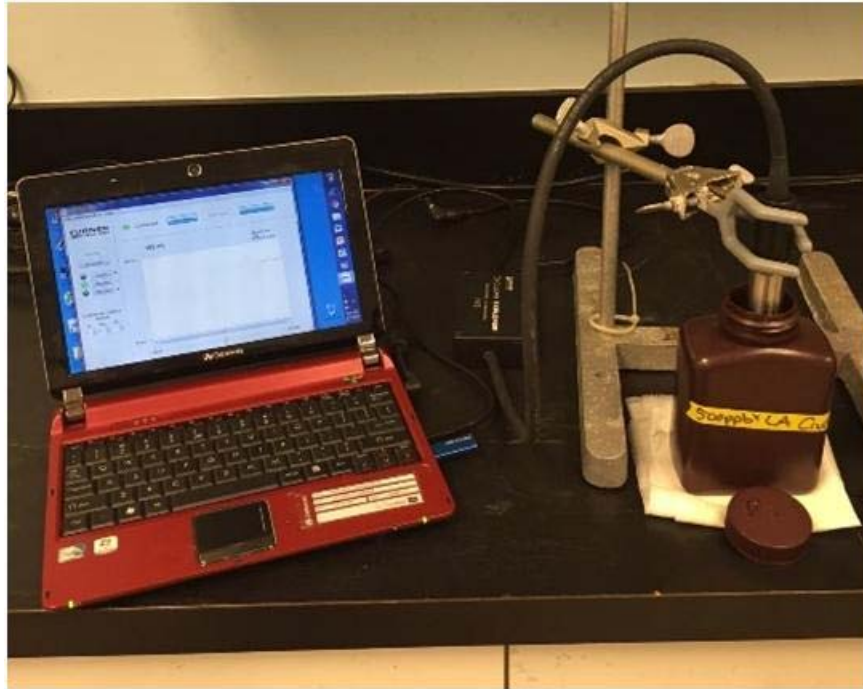


Figure B-2. Cyclops-7 laboratory calibration setup.

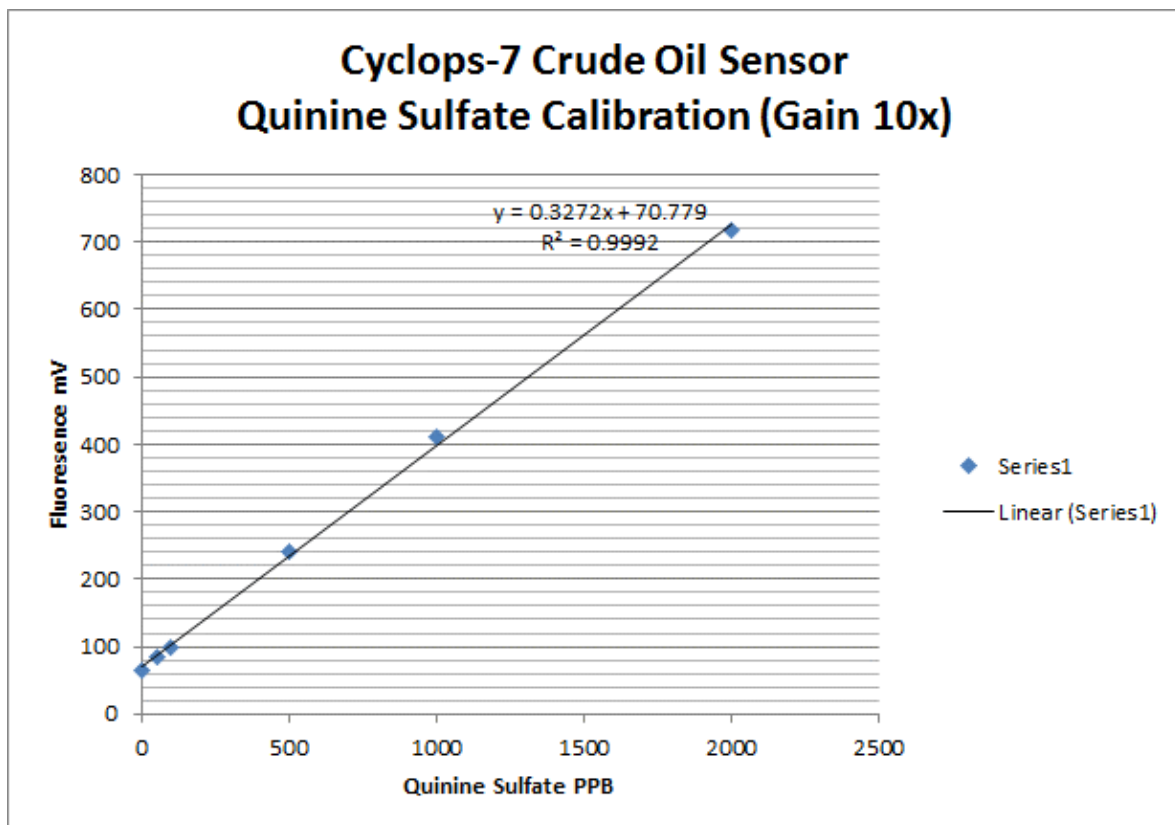


Figure B-3. Example of Cyclops-7 crude oil sensor calibration using quinine sulfate as a fluorescence reference standard.



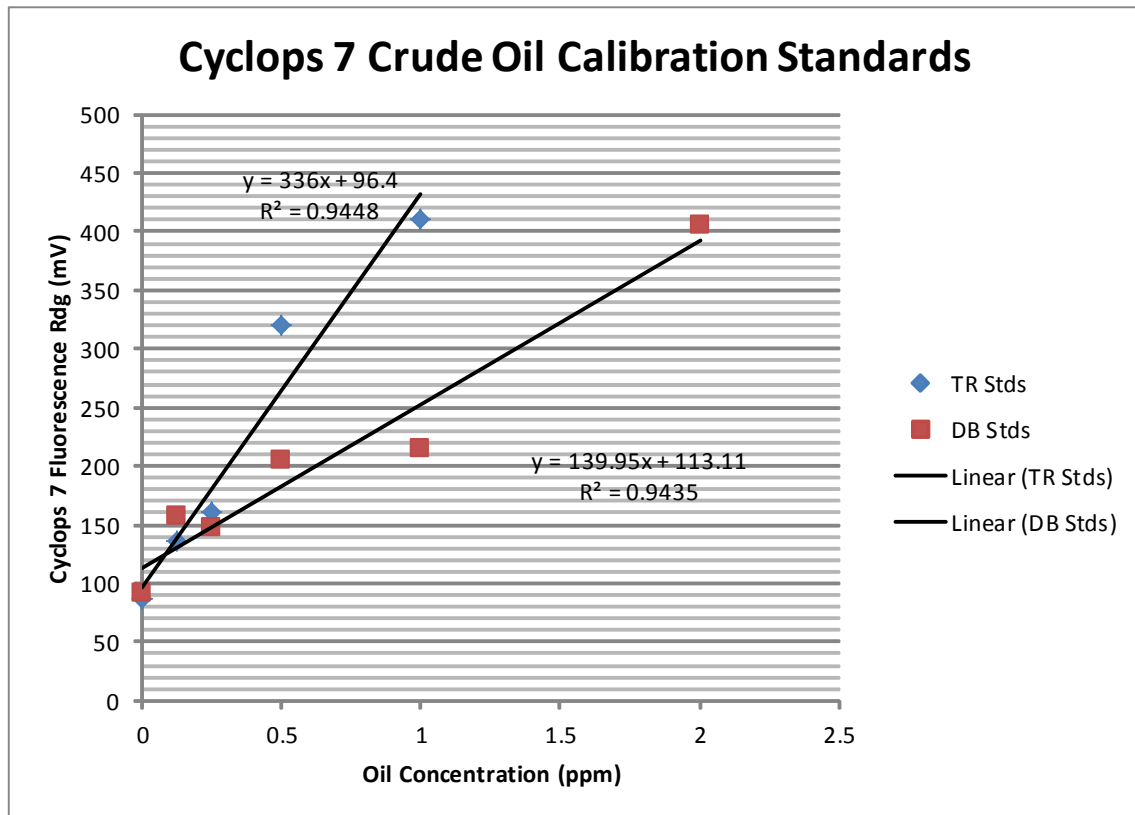


Figure B-4. Sample calculation of Cyclops-7 crude oil sensor calibration using Water Accommodated Fractions (WAF) of Texas Raw Crude and Dilbit Crude oils as fluorescence standards.

- Use the sand mesh sieve set (Figure B-5) to characterize the particle size distribution of the dry sand and sediments used in the experiments.



Figure B-5. Sediment-water-oil mesh sieve set.

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4. Develop, test, and evaluate a laboratory bench-top methodology to prepare and homogeneously mix oil/sediment/water mixtures in 8-liter plastic containers. The goal is to be able to establish a series of experimental treatments with a known gradient of crude oil concentrations in the sediments contained in the experimental containers. The test team evaluated two approaches: a) adding oil to the sediment phase first, mixing dry, and then adding water and mixing the resulting mixture, and b) adding oil to the water phase, and then mixing the resulting mixture. Approach (a) was more successful and adopted for the Demonstration.
5. Test and evaluate a methodology to sample the experimental oil-impacted submerged sediment layer (a core sample) and analyze the concentration of total petroleum hydrocarbons using the Dexsil PetroFlag TPH test kit.
6. Test, characterize, and evaluate the ability of the Cyclops-7 prototype fabricated sensor probe, with mesh screen, to measure the TPH contents of the supernatant and sediment pore waters in the series of experimental containers containing different crude oil/sediment/water mixtures. The calculations used to guide the preparation of these mixtures are shown in Table B-1.
7. Modify sensor probe technology as required to improve performance. Note: the probe was intended as a laboratory prototype, and several changes were made to the design during the testing. Initially the probe, which was made through 3-D printing, fractured due to the force and twisting action required to penetrate the sediment. The successful prototype design included the following changes:
  - a. Shell construction was changed from a porous shell a solid shell build.
  - b. Probe material was changed from ABS plastic to nylon.
  - c. The probe openings for the mesh screen were modified to relieve stress points.

Table B-1. Sample calculation to guide preparation of experimental oil/sediment/water mixtures. Crude oil density is approximately 0.84 grams/ml or 840 mg/ml.

| Example Calculations to Guide Preparation of Experimental Oil-Water-Sediment Mixtures  |                 |                  |                |                             |                             |                 |                        |                        |
|--|-----------------|------------------|----------------|-----------------------------|-----------------------------|-----------------|------------------------|------------------------|
| Weight Oil<br>mg   | Weight Oil<br>g | Volume Oil<br>mL | Wt. Sand<br>kg | TPH Sediment<br>mg/kg (ppm) | TPH Sediment<br>ug/kg (ppb) | Vol. Water<br>L | TPH Water<br>mg/kg ppm | TPH Water<br>ug/kg ppb |
| 0.000  | 0.000000        | 0.000000         | 4.50           | 0.000                       | 0.00                        | 4.50            | 0.00                   | 0.00                   |
| 0.035  | 0.000035        | 0.000042         | 4.50           | 0.008                       | 7.78                        | 4.50            | 0.01                   | 7.78                   |
| 0.175  | 0.000175        | 0.000208         | 4.50           | 0.039                       | 38.89                       | 4.50            | 0.04                   | 38.89                  |
| 0.350  | 0.000350        | 0.000417         | 4.50           | 0.078                       | 77.78                       | 4.50            | 0.08                   | 77.78                  |
| 1.750  | 0.001750        | 0.002083         | 4.50           | 0.389                       | 388.89                      | 4.50            | 0.39                   | 388.89                 |
| 3.500  | 0.003500        | 0.004167         | 4.50           | 0.778                       | 777.78                      | 4.50            | 0.78                   | 777.78                 |
| 7.000  | 0.007000        | 0.008333         | 4.50           | 1.556                       | 1,555.56                    | 4.50            | 1.56                   | 1555.56                |
| 17.500   | 0.017500        | 0.020833         | 4.50           | 3.889                       | 3,888.89                    | 4.50            | 3.89                   | 3888.89                |
| 24.500   | 0.024500        | 0.029167         | 4.50           | 5.444                       | 5,444.44                    | 4.50            | 5.44                   | 5444.44                |
| 35.000   | 0.035000        | 0.041667         | 4.50           | 7.778                       | 7,777.78                    | 4.50            | 7.78                   | 7777.78                |
| 175.000  | 0.175000        | 0.208333         | 4.50           | 38.889                      | 38,888.89                   | 4.50            | 38.89                  | 38888.89               |
| 350.000  | 0.350000        | 0.416667         | 4.50           | 77.778                      | 77,777.78                   | 4.50            | 77.78                  | 77777.78               |
| 1750.000   | 1.750000        | 2.083333         | 4.50           | 388.889                     | 388,888.89                  | 4.50            | 388.89                 | 388888.89              |
| 3500.000   | 3.500000        | 4.166667         | 4.50           | 777.778                     | 777,777.78                  | 4.50            | 777.78                 | 777777.78              |
| 17500.000  | 17.500000       | 20.833333        | 4.50           | 3888.889                    | 3,888,888.89                | 4.50            | 3888.89                | 3888888.89             |
| 35000.000  | 35.000000       | 41.666667        | 4.50           | 7777.778                    | 7,777,777.78                | 4.50            | 7777.78                | 7777777.78             |
| 175000.000   | 175.000000      | 208.333333       | 4.50           | 38888.889                   | 38,888,888.89               | 4.50            | 38888.89               | 38888888.89            |
| 350000.000   | 350.000000      | 416.666667       | 4.50           | 77777.778                   | 77,777,777.78               | 4.50            | 77777.78               | 77777777.78            |
| 1750000.000  | 1750.000000     | 2083.333333      | 4.50           | 388888.889                  | 388,888,888.89              | 4.50            | 388888.89              | 388888888.89           |
| Note: Calculated TPH Sediment and TPH Water concentrations are assuming that all of the added oil is incorporated into the sediment or the water phases. |                 |                  |                |                             |                             |                 |                        |                        |



**Early Laboratory Experimentation:** As part of our earlier laboratory effort developing the SOMS technology we conducted the following:

1. Laboratory characterization and validation of the Cyclops-7 Crude Oil Sensor and Prototype Sediment Probe for detecting Dilbit and other crude oils in sediment pore waters.
2. The development, characterization and validation of a means to create a laboratory-scale concentration-gradient of oil/sediment/water mixtures that could be used to test, evaluate and demonstrate the prototype SOMS.

These activities involved:

### **Cyclops-7 Crude Oil Sensor and Prototype Sediment Probe**

1. Prepared and tested comparative water accommodated fraction (WAF) Calibration Standards for Dilbit, Texas Raw Crude and Louisiana crude oils.
2. Prepared and tested a Fluorescence Reference Standard using Quinine Sulfate.
3. Examined comparative functioning of Cyclops-7 Crude Oil Sensor in and out of the prototype probe housing.
4. Examined potential effect of Fluorescence Quenching of crude oil signals as a function of seawater salinity.
5. Characterized grain size distribution of clean sand being used for the sediment phase.
6. Examined potential effect of turbidity, due to suspended silt, on the Cyclops-7 sensor response.

### **Laboratory-scale concentration-gradient of Oil/Sediment/Water Mixtures**

1. Developed a conceptual framework and concentration ranges for the oil/sediment/water mixtures.
2. Prepared three lab-scale (approximately eight liter) test SOW mixtures: Control (no oil), Dilbit and Texas Raw Crude. Added crude oil to water/sediment, mixed and then allowed to settle. Conducted preliminary tests with the Cyclops-7 and the prototype probe housing.
3. Conducted and evaluated a series of smaller scale (0.5 L) experiments on various methodologies to prepare and effectively mix crude oil with water and/or sediment.

A summary of these Early Laboratory SOMS Experimentation Results was presented to the USCG in a slide presentation on 30 March. We experienced, and overcame, experimental challenges related to the density and hydrophobic nature (stickiness) of the crude oils. Good progress was made on the laboratory characterization and validation of the Cyclops-7 Crude Oil Sensor and prototype probe towards the goal of measuring the TPH levels of Dilbit and other crude oils in sediment pore waters. We then continued to focus on the development, characterization and validation of a means to create a laboratory-scale concentration-gradient of oil/sediment/water mixtures to test, evaluate and demonstrate the prototype SOMS.



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### APPENDIX C. PROOF OF CONCEPT PRE-DEMONSTRATION EXPERIMENTS

**Introduction:** This section describes the laboratory work accomplished at SubChem after the 30 March on-site review meeting. The experimental observations confirmed the primary hypothesis behind the envisioned SOMS methodology; the concentration of TPH in crude oil impacted sediments is directly related to the concentration of crude oil detected in the sediment pore waters. Applying this mathematical relationship along with the measurement of one of the two parameters, allows the prediction of the other parameter.

#### Work Completed in April

Our primary tasks, listed below, were completed.

- 1) **SOMS Lab-Scale Experimental Gradient:** Developed and implemented a procedure to prepare a series of laboratory-scale oil/sediment/water mixtures with a defined concentration gradient (ppm range) of crude oil in the sediments. The experimental containers were ~8-liter volume, with 4.5 kg sediment (sand) and 4.5 kg of seawater (~30 ppt). Dilbit (DB) and Texas Raw Crude (TR) were the two crude oils being tested. The amount of crude oil added varied from ~1-52 grams per container, which is equivalent to ~200 to ~10,000 ppm crude oil in the sediments.
- 2) **Dexsil PetroFlag TPH Analytical Test Kit:** Used the test kit to measure and establish the TPH concentration in the sediment phase of the experimental treatments ([http://www.dexsil.com/products/detail.php?product\\_id=23](http://www.dexsil.com/products/detail.php?product_id=23)). Compared the PetroFlag results for TPH with expected values, based on the actual weight of oil added to the sediment in each experimental container.
- 3) **Turner Designs Cyclops-7 Crude Oil Probe:** Calibrated the Cyclops-7 fluorescence probe for the determination of each type of oil (TR and DB) by fluorescent measurements of the water accommodated fraction (WAF) of a separate series of prepared oil/water standards. Calculated the calibration coefficients for each type of crude oil.
- 4) **The Prototype SOMS Probe:** Used the calibrated Cyclops-7 sensor, installed inside our custom-designed SOMS probe, to measure the fluorescence and determine the concentration of oil in the WAF of the surficial waters and the sediment pore waters, in each experimental treatment. The Cyclops-7 calibration coefficients, calculated above, were used to calculate the concentration of oil in the surficial waters and the sediment pore waters.
- 5) **SOMS Probe Lab-Scale Proof-of Concept:** Compared, correlated, and established a predictive relationship between the PetroFlag results for TPH in the sediments and the SOMS Probe results for oil in the sediment pore water WAF. This was done for all the experimental treatments containing either Texas Raw or Dilbit crude oils.

#### Summary of Results

- 1) **SOMS Lab-Scale Experimental Gradient:** The chemical and physical properties of crude oils, especially Dilbit, cause unpredictable problems when they are accidentally released into the marine





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environment (Polaris Applied Sciences, Inc., 2013). We also found this to be true in the laboratory, complicating our initial approach and plans to make a series of small-scale experimental oil/sediment/water mixtures.

**The Problem:** For our initial approach (back in February) - we first added the sediment (4.5 kg) and next the water (4.5 L) to the plastic containers. Then we carefully added the known aliquot of crude oil, measured by weight. We then thoroughly mixed the oil/sediment/water mixture using a high-speed paint mixer. It was immediately apparent that this procedure did not work well – much of the oil (particularly Dilbit) stayed in the water phase, absorbed on the plastic container wall. The Dilbit also absorbed onto the plastic mixer and container (Figure C-1).



Figure C-1. Dilbit absorbed onto the plastic mixer and container.

**The Solution:** After a series of small-scale (1 liter) sediment-oil-water mixing experiments, it was determined that the preferred approach, to meet our experimental goal, was to add the “weighed” crude oil aliquot directly into the 4.5 kg of dry sand, in the experimental container (Figure C-2). A spoon was then used to cover the crude oil with some of the sand. In essence, a small tar ball was formed, comprised of sand and crude oil. Then the mixer was used to break up the tar ball into tiny pieces and homogenously blending the oil and sand mixture. You could visibly see the color of the sand get darker as the crude oil was evenly mixed into it. The crude oil did not stick to the plastic mixer. Before adding seawater, 2-10 g samples of the dry sediment-oil blend were taken and stored for later analysis by the PetroFlag TPH test kit. Clean seawater (4.5 L of Sargasso Seawater diluted to 30 o/oo with DI water) was then added to the containers, and the oil/sediment/water mixture was thoroughly mixed with the plastic mixer.



Figure C-2. “Weighed” crude oil aliquot directly into the 4.5 kg of dry sand, in the experimental container.



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Thirteen experimental containers were prepared in this manner with varying concentrations of Texas Raw or Dilbit crude oils. The nominal concentrations of crude oil added were 0, 500, 1000, 1500, 2000, and 3000 ppm, for both the Texas Raw and the Dilbit crude oils. To extend the observational range, two containers were also prepared for Dilbit Crude with 5000 and 10,000 ppm oil additions. The suspended sediment in the well-mixed containers were allowed to settle for several days before taking wet sediment samples for PetroFlag TPH analyzes or making in situ measurements of oil in the sediment pore water (WAF) using the SOMS Probe.

- 2) **Dexsil PetroFlag TPH Analytical Test Kit:** This convenient test kit uses an EPA approved methodology (U.S. EPA SW-846 Method 9074) to rapidly measure Total Petroleum Hydrocarbons (TPH) in sediments (Figure C-3, Figure C-4). It works on dry and wet sediment samples, but sample weight corrections need to be made for sediment samples containing moisture. Initially, some laboratory tests were conducted to evaluate the PetroFlag test kit's ability to accurately measure Texas Raw and Dilbit crude oils. According to this methodology, different types of oil have different Dilbit Response Factors (RF's)," ranging from 1-15. Before measuring the larger-scale experimental samples, small test calibration samples were prepared with dry sand and known amounts (ppm range) of either Texas Raw or Dilbit crude oil. Using this methodology, it was determined that the appropriate RF for Texas Raw Crude was 10 and the appropriate RF for Dilbit was 3.2. This means that the PetroFlag signal response for Dilbit Crude Oil was quantifiably lower than that Texas Raw Crude.

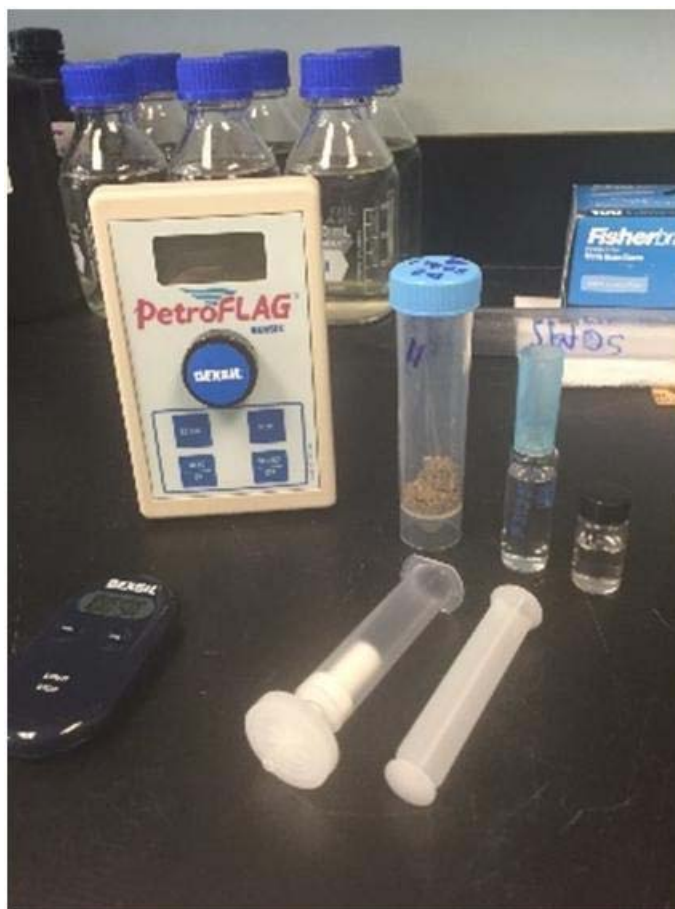


Figure C-3. Dexsil PetroFlag TPH Analytical Test Kit.



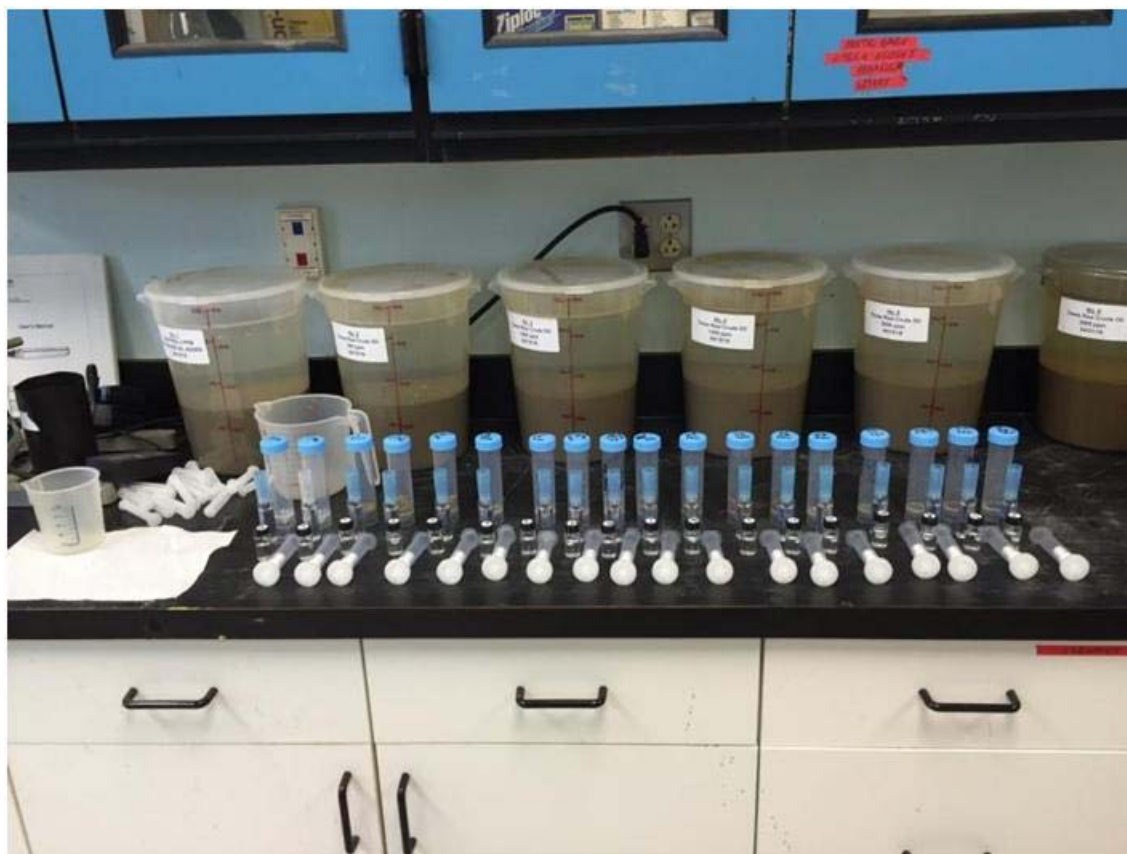


Figure C-4. Dexsil PetroFlag test kits staged for sample collection.

The Dexsil PetroFlag TPH test kit was used to analyze TPH in both “dry” (oil/sediment samples collected before adding water) and “wet” (oil/sediment samples collected after water was added and mixed into the containers) core samples. The results for dry and wet sediments are shown in the following two graphs (Figure C-5 and Figure C-6) for both Texas Raw Crude and Dilbit crude oils. In both cases, there were good correlations between known oil additions and measured oil concentrations. The concentrations found in dry and wet sediments were statistically similar, indicating that most of the crude oil added to the sediments, remained there – even after suspension into the water by mixing. These PetroFlag measurements document that we have attained our goal and created a series of 13 oil/sediment/water mixtures with a known gradient in the sedimentary concentrations of either Texas Raw Crude or Dilbit crude oils.



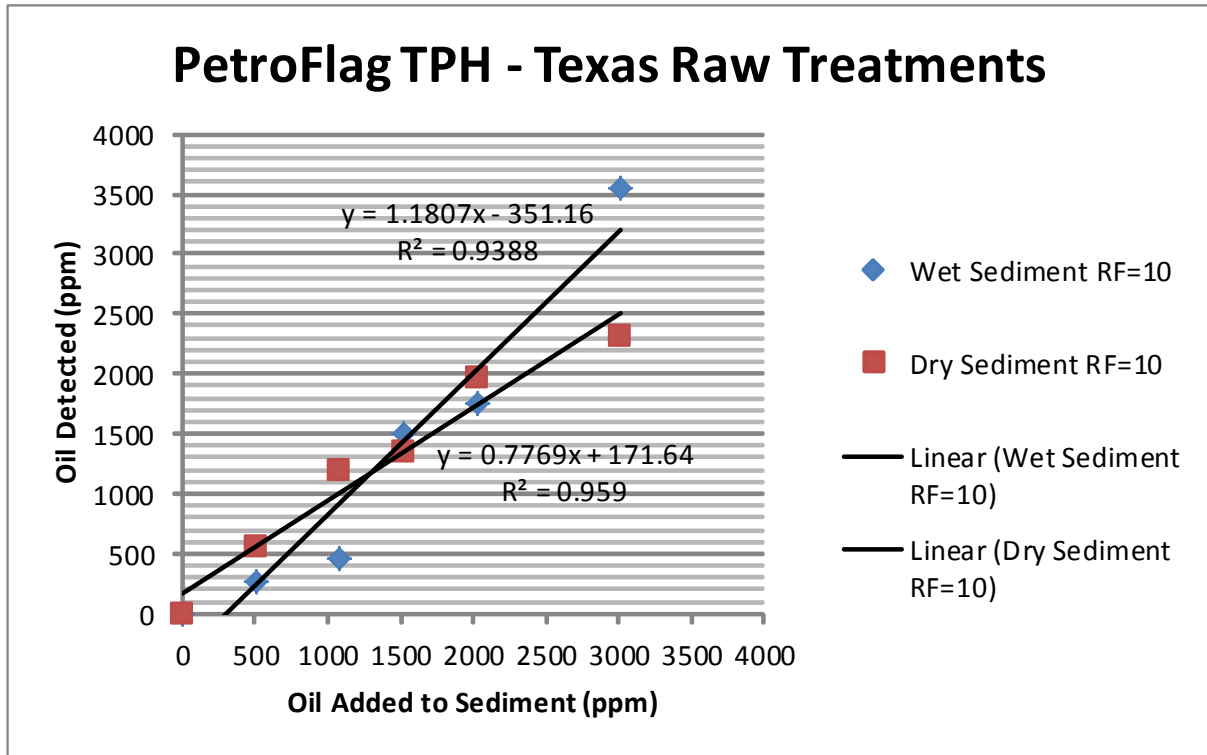


Figure C-5. Texas Crude absorbed onto the plastic mixer and container.

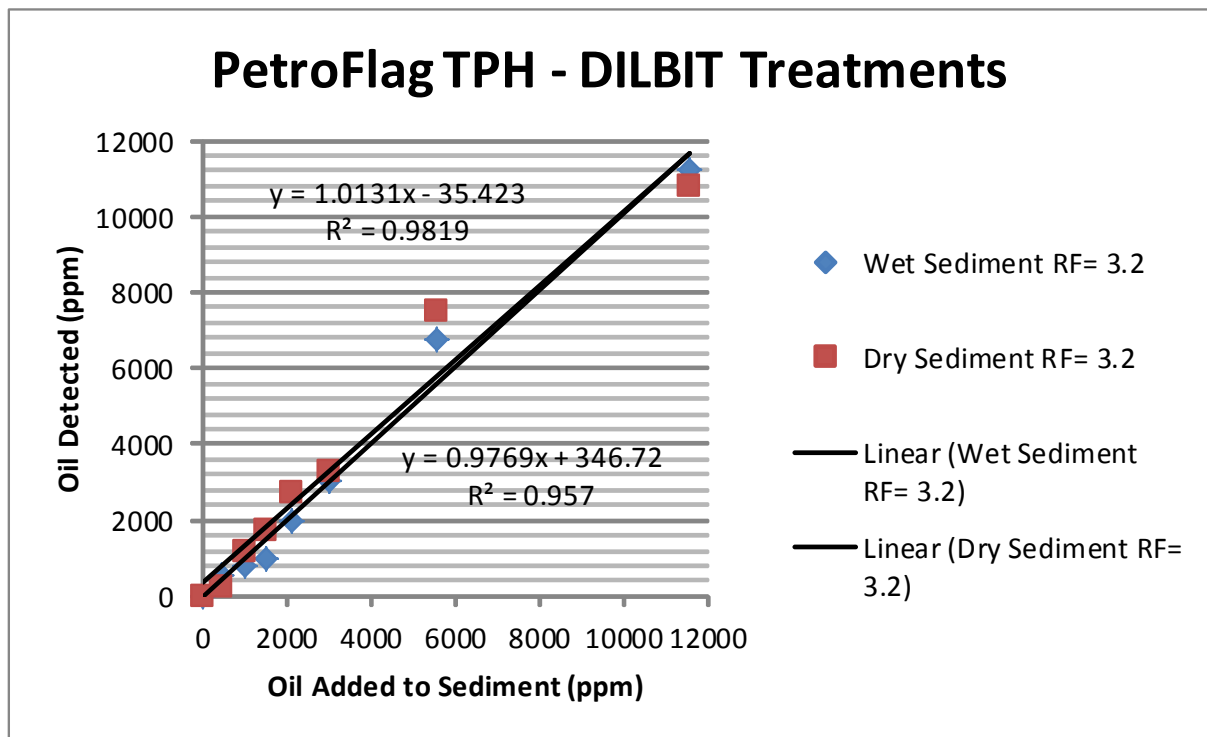


Figure C-6. Dilbit absorbed onto the plastic mixer and container.



- 3) **Turner Designs Cyclops-7 Crude Oil Probe:** A separate series of oil/water standards were prepared by adding known, weighed, amounts of crude oil to clean Sargasso seawater, contained in 1-liter dark plastic bottles. Since the Texas Raw Crude and Dilbit crude oils are not completely solubilized by the seawater, these standards represent the WAF of the two crude oils. The Cyclops-7 fluorescence probe was used to make fluorescent measurements of the WAF of the two separate concentration series (TR and DB) of prepared oil/water standards (Figure C-7). The Cyclops-7 probe has an overall analog output of 0-5000 mV and three selectable ranges (1X, 10X and 100X). 100X is the most sensitive. The intermediate 10X range is most commonly used, and was used for these measurements. One example of the results obtained from these measurements are shown in the following graph (Figure C-8) of Oil Concentration (ppm) versus Fluorescence Reading (mV). The linear calibration coefficients calculated for each type of crude oil are also shown.

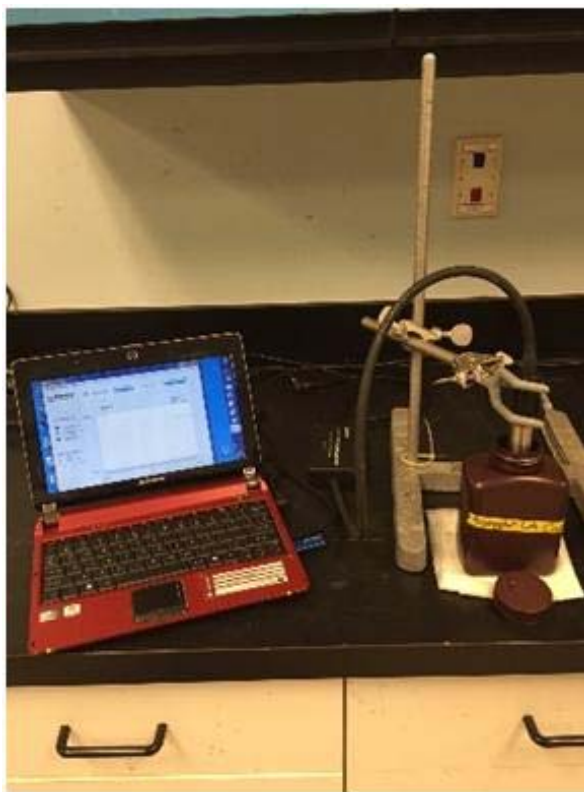


Figure C-7. Testing prepared oil/water standards.



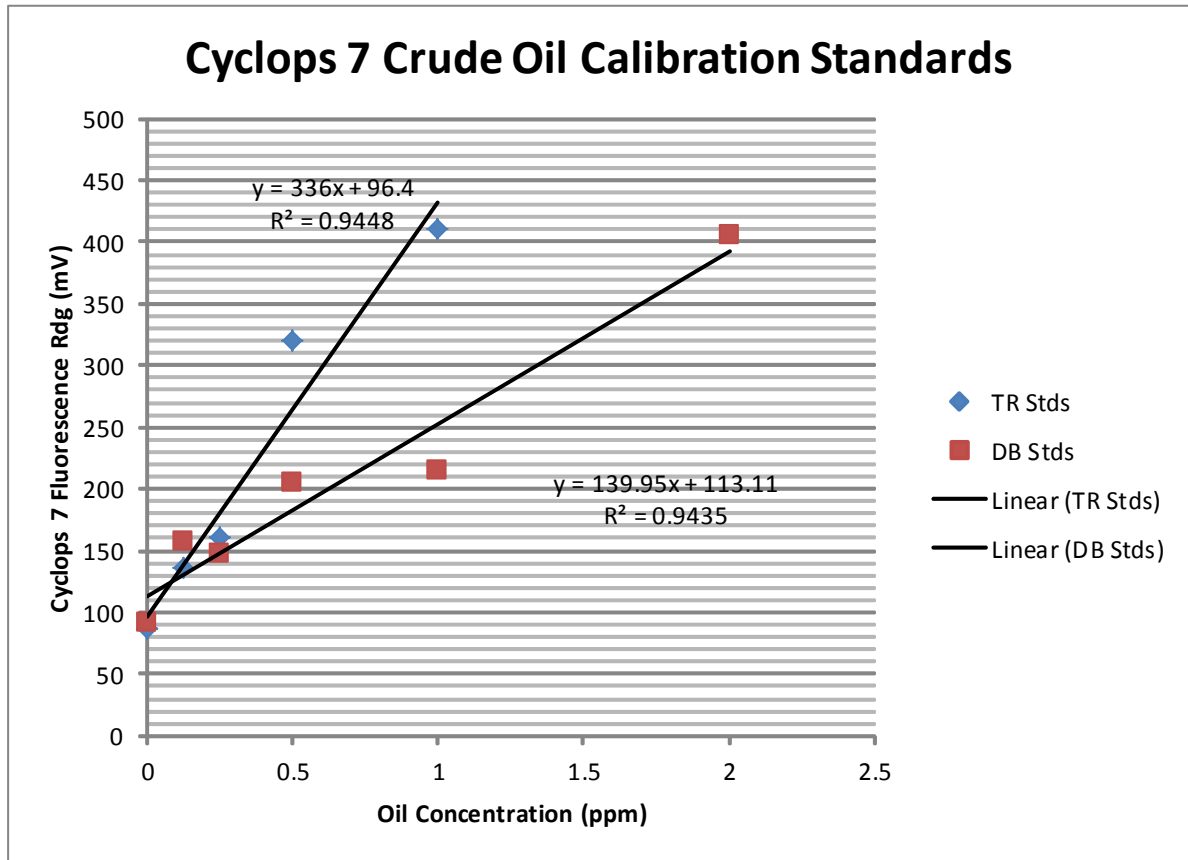


Figure C-8. Oil Concentration (ppm) versus Fluorescence Reading (mV).

As can be seen by comparing the slopes of the two linear regression lines in the graphs, the WAF of Texas Raw Crude has a higher Cyclops-7 fluorescence response factor than the WAF of Dilbit crude oil. These oil-specific calibrations were used for the calculation of the concentration of crude oil in experiments using the SOMS probe. Earlier calibration tests demonstrated that the Cyclops-7 probe gave equivalent fluorescent readings when it was installed in the SOMS Probe housing.

- 4) **The Prototype SOMS Probe:** The calibrated Cyclops-7 probe was installed inside our custom-designed probe, and used to measure the fluorescence and determine the concentration of crude oil in the WAF of first, the surficial waters and second, the sediment pore waters, in each of the 13 experimental treatments (Figure C-9). The Cyclops-7 Explorer data acquisition software was used to record the fluorescence readings (mV) as the SOMS Probe was inserted into the surficial waters and then into the sediments.



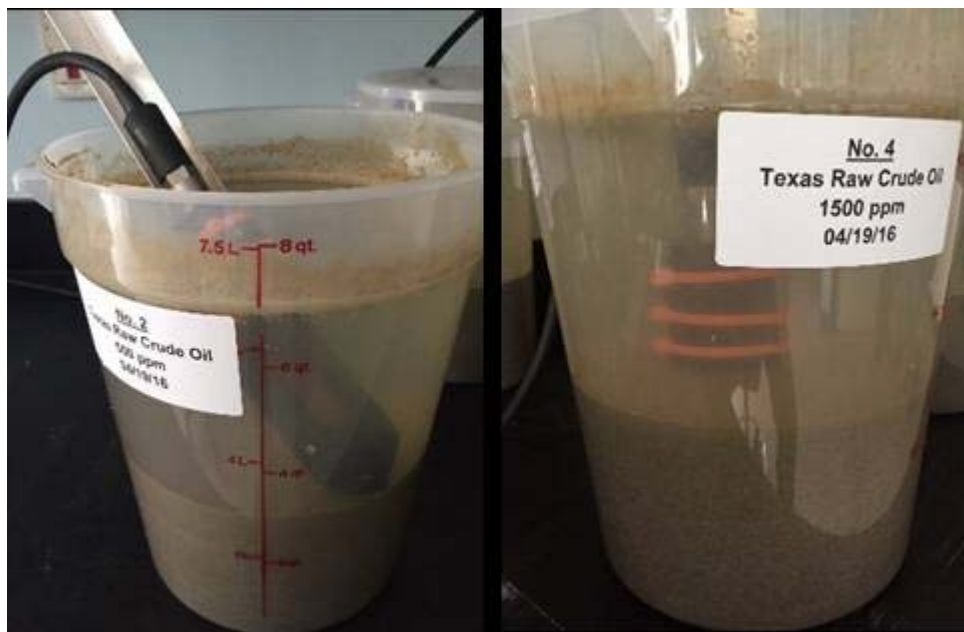


Figure C-9. Measuring fluorescence in the surficial waters (left) and the sediment pore waters (right).

The SOMS Probe was very responsive, and stable fluorescence readings were obtained quickly (one to three minutes) after penetration of the probe into the sediment. The Cyclops-7 calibration coefficients (3), and stable fluorescence readings, were used to calculate the concentration of oil in the WAF that comprised the surficial waters and the sediment pore waters, for all 13 experimental containers. All 13 experimental containers could be measured, in this manner, in about 1 hour.

The following two graphs show the results obtained with the Prototype SOMS Probe for the Texas Raw Crude experimental treatments. The results are reported as 1) the SOMS Probe fluorescence readings (Figure C-10) and 2) the calculated WAF pore water oil concentrations (Figure C-11) (Y-Axis), versus the TPH (Oil) levels (X-Axis) determined in the sediments by the PetroFlag test kit on the sediments (samples collected after mixing with the seawater).





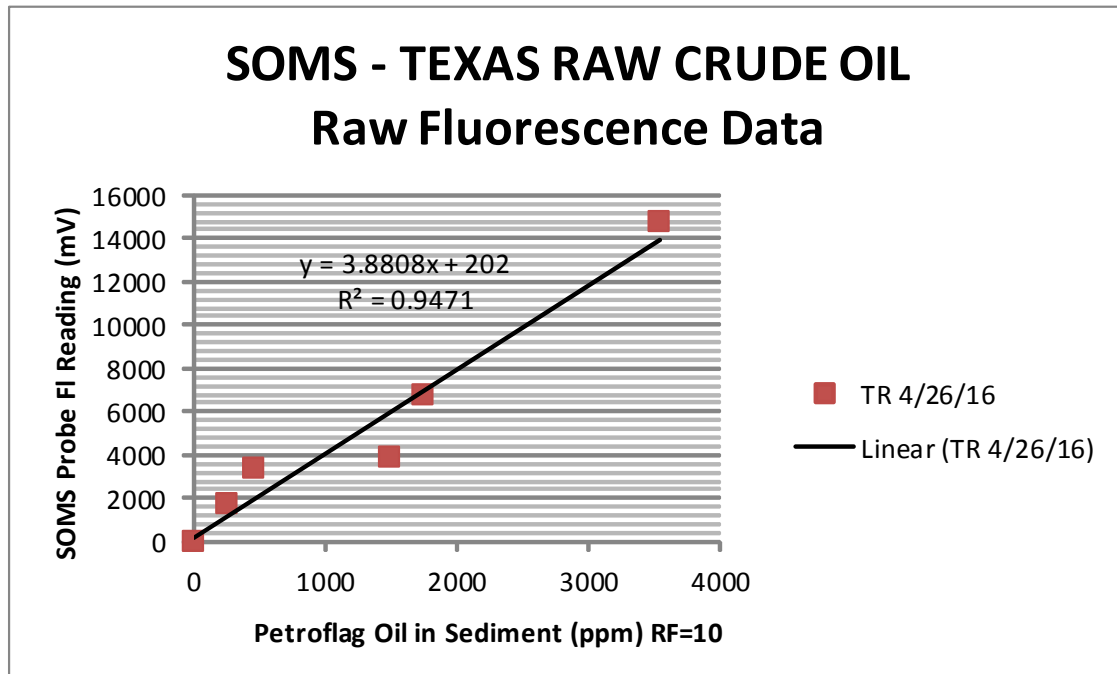


Figure C-10. Probe fluorescence readings.

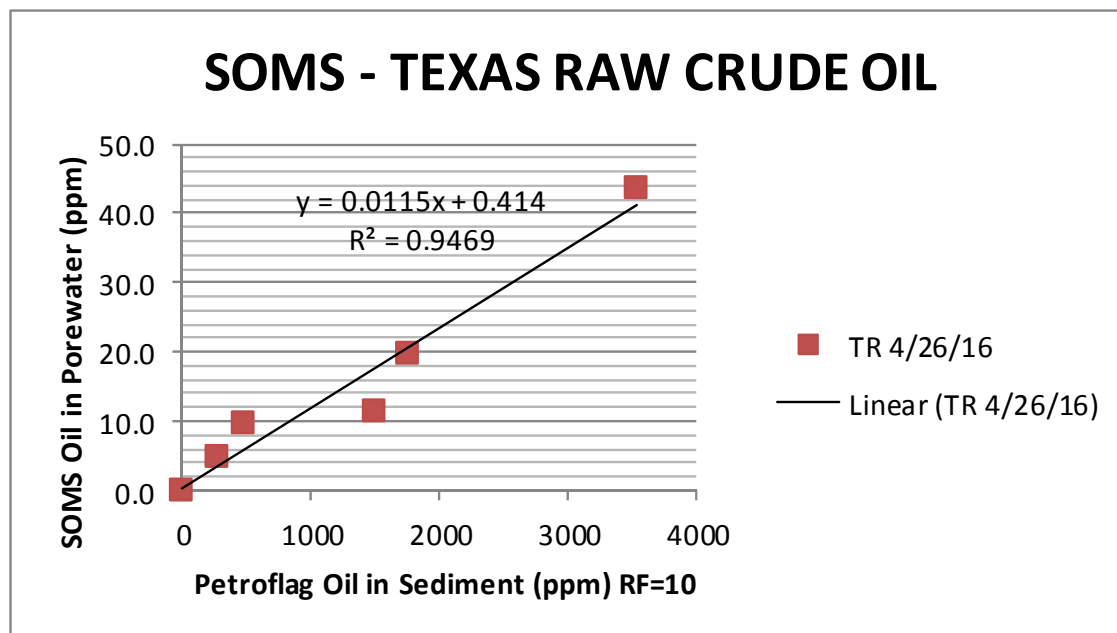


Figure C-11. Calculated WAF pore water oil concentrations.

The following two graphs show the results obtained with the Prototype SOMS Probe for the Dilbit experimental treatments. The results are reported as 1) the SOMS Probe fluorescence readings (Figure C-12) and 2) the calculated WAF pore water oil concentrations (Figure C-13) (Y-Axis), versus the TPH (Oil) levels (X-Axis) determined in the sediments by the PetroFlag test kit on the sediments (samples collected after mixing with the seawater).



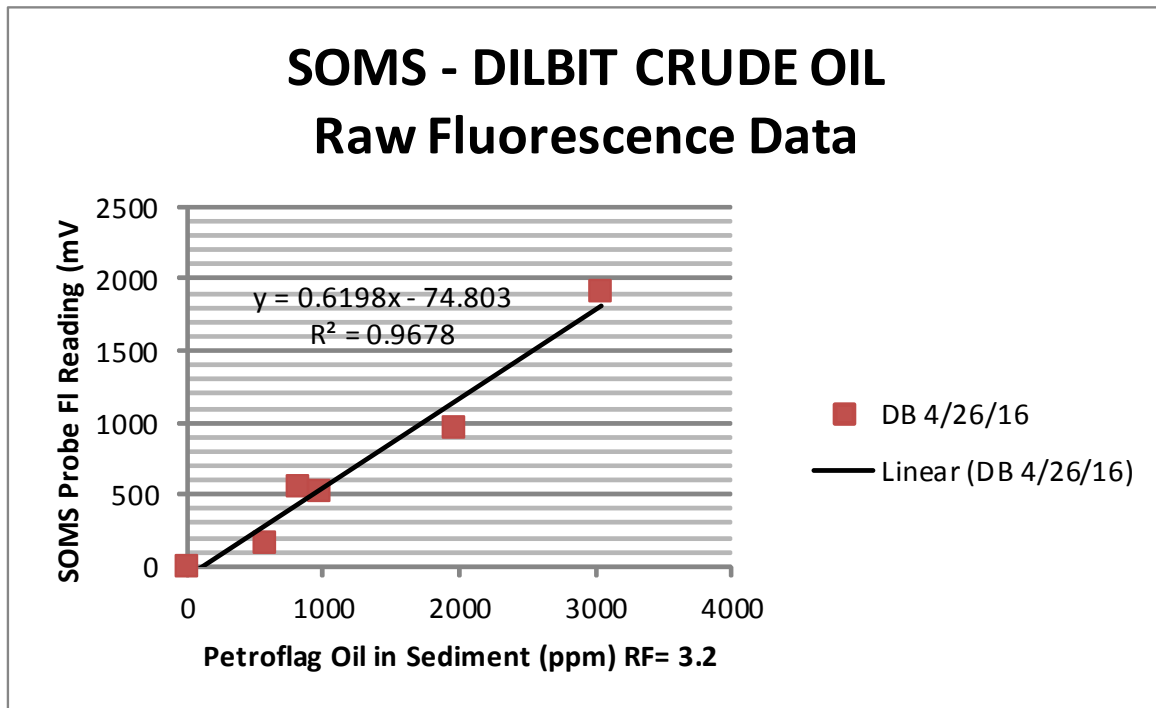


Figure C-12. Probe fluorescence readings.

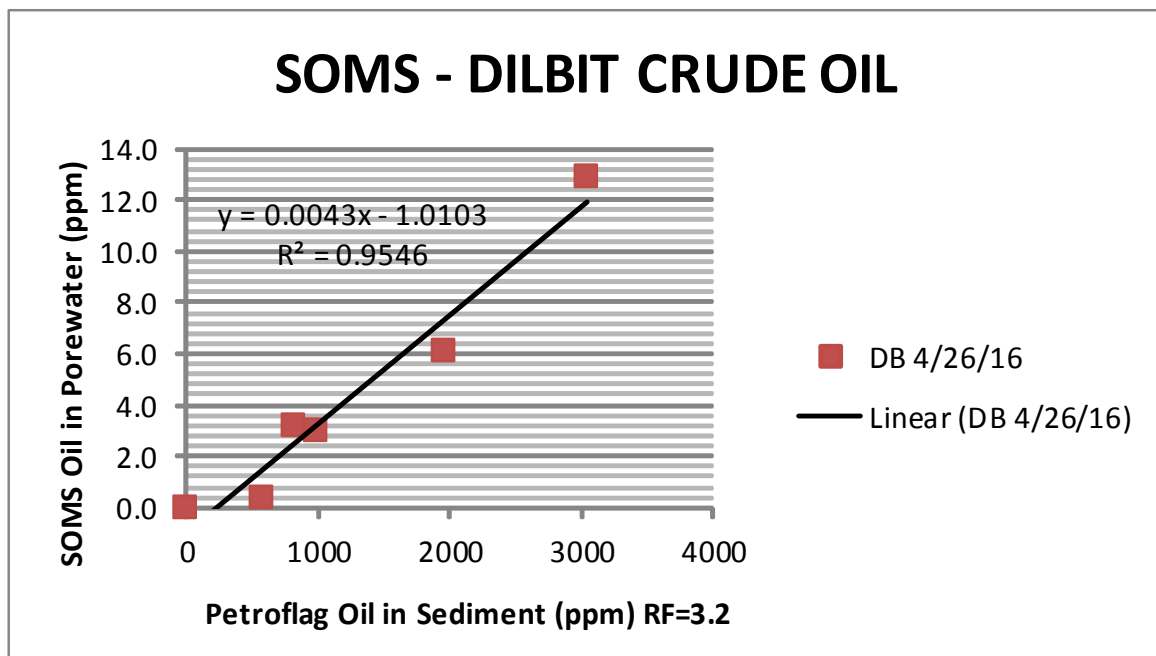


Figure C-13. Calculated WAF pore water oil concentrations.



**SOMS Probe Lab-Scale Proof-of Concept:** The experimental results obtained and reported in the previous four sections allow us to compare, correlate and establish the relationship that exists between the PetroFlag results for TPH in the sediments (2) and the SOMS Probe results (4) for oil in the sediment pore waters (WAF). This was done for all the experimental treatments containing either Texas Raw Crude or Dilbit. Figure C-14 and Figure C-15 use these new SOMS Probe oil-specific predictive relationships, to compare the concentration of oil in the experimental sediments, as determined by the Prototype SOMS Probe with that determined with the PetroFlag Test Kit (which agrees with the known oil additions). The two graphs shown below demonstrate the 1:1 linear correlation ( $r^2 > 0.95$ ) obtained between the two independent measurement techniques, 1) the Prototype SOMS Probe (Y-axis) and 2) the PetroFlag Test Kit (X-Axis) for the total petroleum hydrocarbon (TPH) concentrations of Texas Raw Crude (Figure C-14) and Dilbit (Figure C-15) in the sediments from the 13 different experimental treatments.

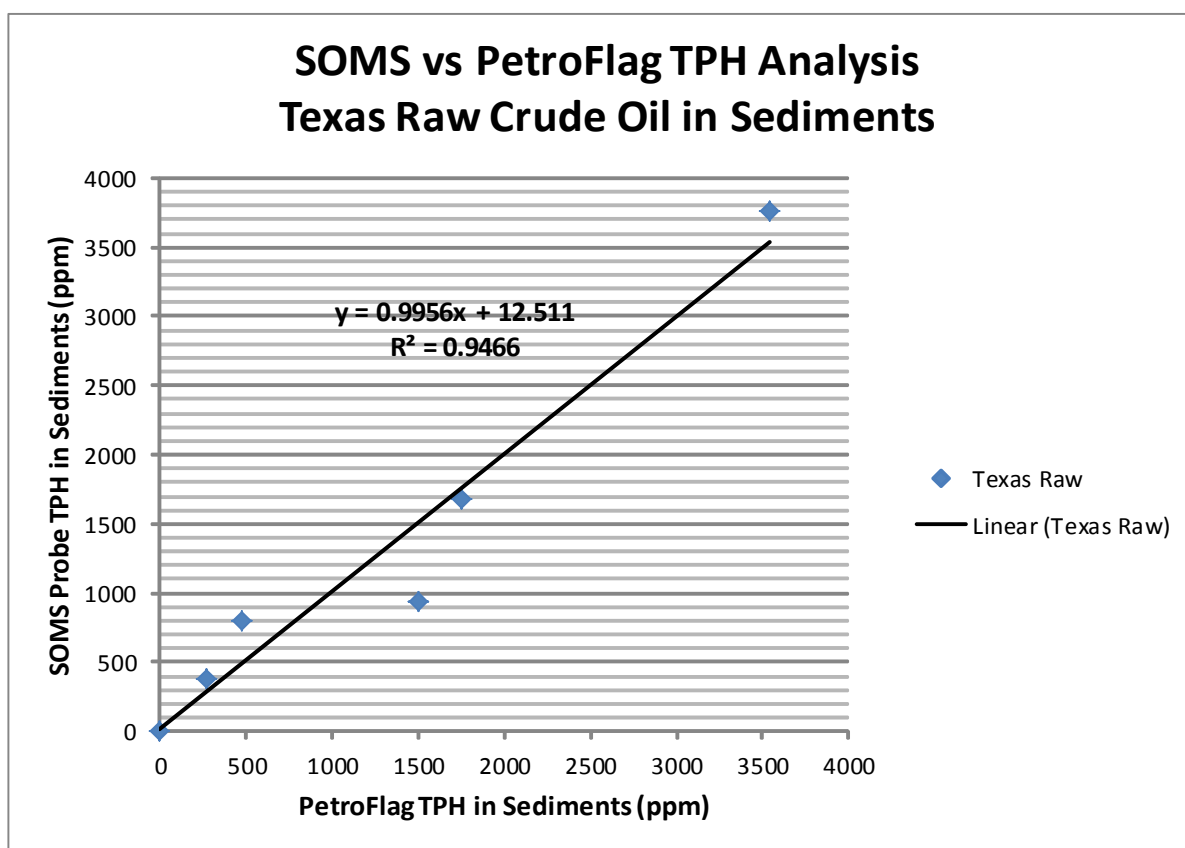


Figure C-14. Calculated WAF pore water oil concentrations.



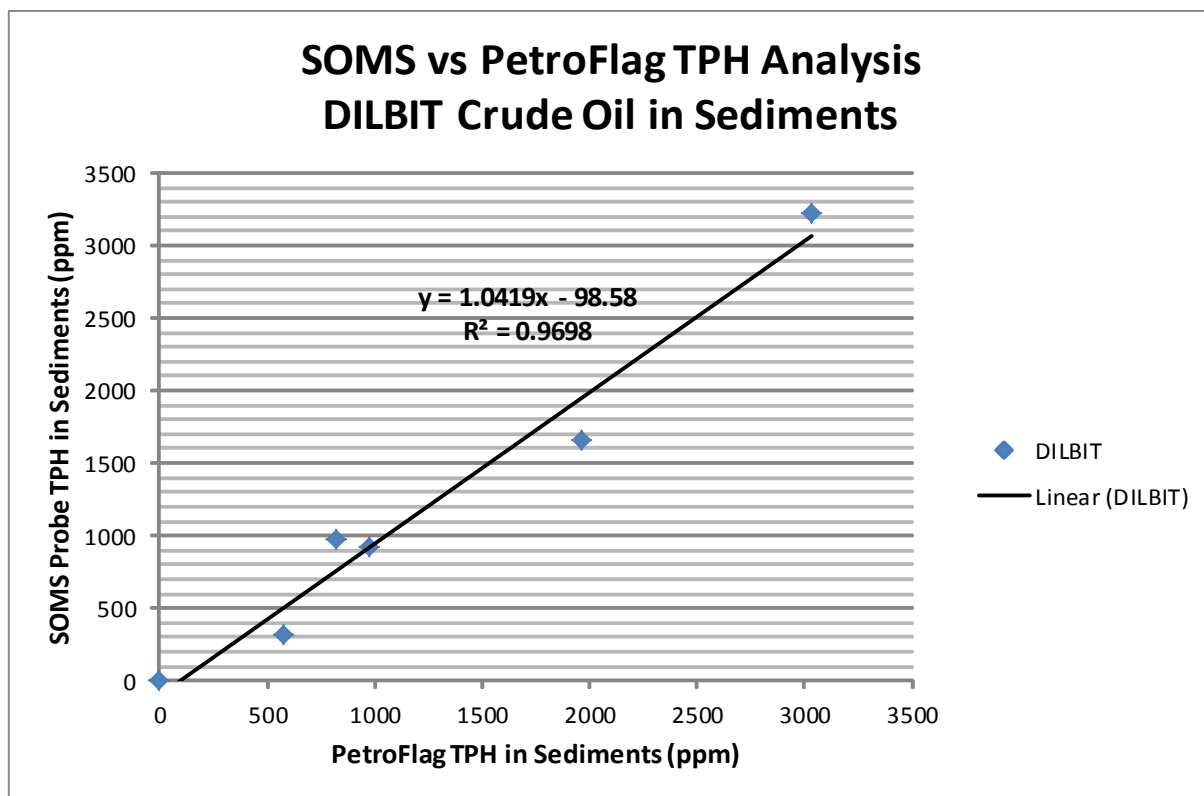


Figure C-15. Calculated WAF pore water oil concentrations.

### Summary:

As stated earlier, these proof-of concept results were very encouraging because the experimental observations confirmed the primary hypothesis behind the envisioned SOMS methodology; the concentration of total petroleum hydrocarbons (TPH) in crude oil impacted sediments is directly related to the concentration of crude oil detected in the sediment pore waters. Applying this mathematical relationship along with the measurement of one of the two parameters, allows the prediction of the other parameter.

Thirteen experimental containers containing layers of sediment (sand) and seawater were carefully prepared and blended with the additions of varying concentrations of Texas Raw Crude or Dilbit. The known (weighed) incremental additions of crude oil to the sediments ranged from zero to 10,000 ppm. The PetroFlag measurements of TPH in these sediments demonstrated that we had attained our goal and created a series of 13 oil/sediment/water mixtures with a known gradient in the sedimentary concentrations of either Texas Raw Crude or Dilbit.

The calibrated Cyclops-7 Crude Oil probe was installed inside our custom-designed SOMS Probe Housing, and used to measure the fluorescence and determine the concentration of crude oil in the WAF of first, the surficial waters and second, the sediment pore waters, in each of the 13 experimental treatments. For all of the 13 experimental treatments, for both Texas Raw Crude and Dilbit, there was a strong linear relationship between the concentration of oil in the sediments and the concentration of oil in the WAF of the sediment pore waters. Again, these experimental observations confirm the primary hypothesis behind the envisioned SOMS methodology. The concentration of oil in the sediments was verifiable from both the known oil additions to the sediments, and the PetroFlag TPH Analytical measurements.



## Underwater Sediment Sampling Research

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The linearly correlated data obtained allowed us to determine the SOMS Probe oil-specific predictive relationships between the Prototype SOMS Probe measurements in sediment pore waters and the total concentration of Texas Raw Crude or Dilbit in the sediment.

### **SOMS Probe Oil-Specific Predictive Relationships:**

**Texas Raw Crude: Sediment TPH (ppm) = 87.0 x (SOMS WAF Pore water, ppm) - 36 (ppm)**

**Dilbit Crude: Sediment TPH (ppm) = 232.6 x (SOMS WAF Pore water, ppm) + 235 (ppm)**



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### APPENDIX D. PROOF OF CONCEPT POST-DEMONSTRATION EXPERIMENTS

During the demonstration, differences between the expected measurements and the 1 June demonstration results raised questions about the repeatability of the SOMS measurements over time. This was particularly true for the higher concentration mixtures of Texas Raw Crude and Dilbit. To help answer these questions, the test team conducted additional work described below. Some of the Figures are in the main body of the report and not repeated in this appendix.

A time-series of oil measurements on the original 17 treatments by both the PetroFlag and SOMS methodologies, was reviewed, and additional experiments were conducted to help evaluate the potential variation in SOMS measurements over time. If different oil measurement results were observed, the test team attempted to determine if these differences were due to either: 1) Changes in the PetroFlag or SOMS oil measurement techniques, or 2) Actual changes, over the time span of observations (two to four months), in the oil distribution or concentration in the laboratory experimental containers.

**SOMS Experimental History:** Table D-1(repeat of Table 5) shows the time-series of sample preparations, PetroFlag sampling, SOMS Probe measurements and other operations involving potential disturbance of the sediments and changes to oil concentrations. The seventeen SOMS experimental Sediment-Water-Oil treatments were prepared in two groups.

The first group of four treatments was prepared on 19 February. Crude oil was added into the seawater overlying the sediment in the containers. This oil addition technique did not work well – too much oil stuck to container walls. Figure D-1 shows the Control, TR ~390 ppm and DB ~390 ppm treatments a few days after preparation on 19 February. Note the excessive oil residue stuck to the Dilbit container wall (far right).



Figure D-1. Control, TR ~390 ppm and DB ~390 ppm treatments.



## Underwater Sediment Sampling Research

Table D-1. Time-series of sample preparations, PetroFlag sampling, SOMS Probe measurements and other operations involving potential disturbance of the sediments.

| SOMS Experimental Treatments Sediment Disturbance Timeline |  |                    |           |  |
|--|--|--------------------|-----------|--|
| DATE   | Operation  | Sediment Disturbed | # Samples | Experimental Treatments                              |
| 2/19/2016  | Expt Container Prep & Mix                        | yes                | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |
| 3/24/2016  | SOMS Probe - Initial Sediment Test               | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/13/2016  | SOMS Probe - FL of surface & sed. pore waters    | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/13/2016  | PetroFlag Core Samples- Extract and Analyze      | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/19/2016  | Expt Container Prep & Mix - No H2O               | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/20/2016  | PetroFlag Core Sample (Dry Sediment)             | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/21/2016  | Expt Container Prep & Mix - Added H2O            | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/22/2016  | Cyclops 7 to measure FL of filtered supernatants | no                 | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/22/2016  | SOMS Probe - FL of surface water                 | no                 | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/22/2016  | SOMS Probe - FL of surface & sed. pore waters    | yes                | 11        | Control B, TR 2-6, DB 7-11 ~0-3000 ppm oil           |
| 4/25/2016  | Expt Container Prep & Mix - Added H2O            | yes                | 2         | DB 12&13, ~5000 & ~ 10,000 ppm oil                   |
| 4/26/2016  | SOMS Probe - FL of surface & sed. pore waters    | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 4/26/2016  | SOMS Probe - FL of surface & sed. pore waters    | yes                | 3         | Control A, TR and DB ~390 ppm oil                    |
| 4/28/2016  | PetroFlag Core Sample (Wet Sediment)             | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 5/2/2016   | Analyze PetroFlag from 4/28/16                   | no                 | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 5/31/2016  | SOMS Probe - FL of surface & sed. Pore waters    | yes                | 1         | Pre-Demo recheck TR 4 ~1500 ppm oil                  |
| 6/1/2016   | SOMS Probe - FL of surface & sed. Pore waters    | yes                | 4         | USCG DEMO: TR 5, TR 6, DB 9, DB 11                   |
| 6/8/2016   | SOMS Probe - FL of surface & sed. Pore waters    | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 6/8/2016   | SOMS Probe - FL of surface & sed. Pore waters    | yes                | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |
| 6/14/2016  | PetroFlag Core Sample (Wet Sediment)             | yes                | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 6/14/2016  | PetroFlag Core Sample (Wet Sediment)             | yes                | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |
| 6/14/2016  | Expt Container Re-Mix                            | yes                | 7         | Control B, TR 4,5,6, DB 9,10,11 ~1500 - 3000 ppm oil |
| 6/16/2016  | SOMS Probe - FL of surface & sed. Pore waters    | yes                | 7         | Control B, TR 4,5,6, DB 9,10,11 ~1500 - 3000 ppm oil |
| 6/16/2016  | Analyze PetroFlag from 6/14/16                   | no                 | 13        | Control B, TR 2-6, DB 7-13 ~0-10,000 ppm oil         |
| 6/16/2016  | Analyze PetroFlag from 6/14/16                   | no                 | 4         | Control A, NB Beach, TR and DB ~390 ppm oil          |

The four samples prepared on 19 February (Figure D-2) included:

- 1) Control A: with Commercial Sand, Sargasso Seawater and no oil added.
- 2) Texas Raw Crude (Target 390 ppm) added to Sargasso Seawater and Commercial Sand.
- 3) Dilbit (Target 390 ppm) added to Sargasso Seawater and Commercial Sand.
- 4) Narragansett Bay: Real Beach Sand and Bay Water, with no added oil.



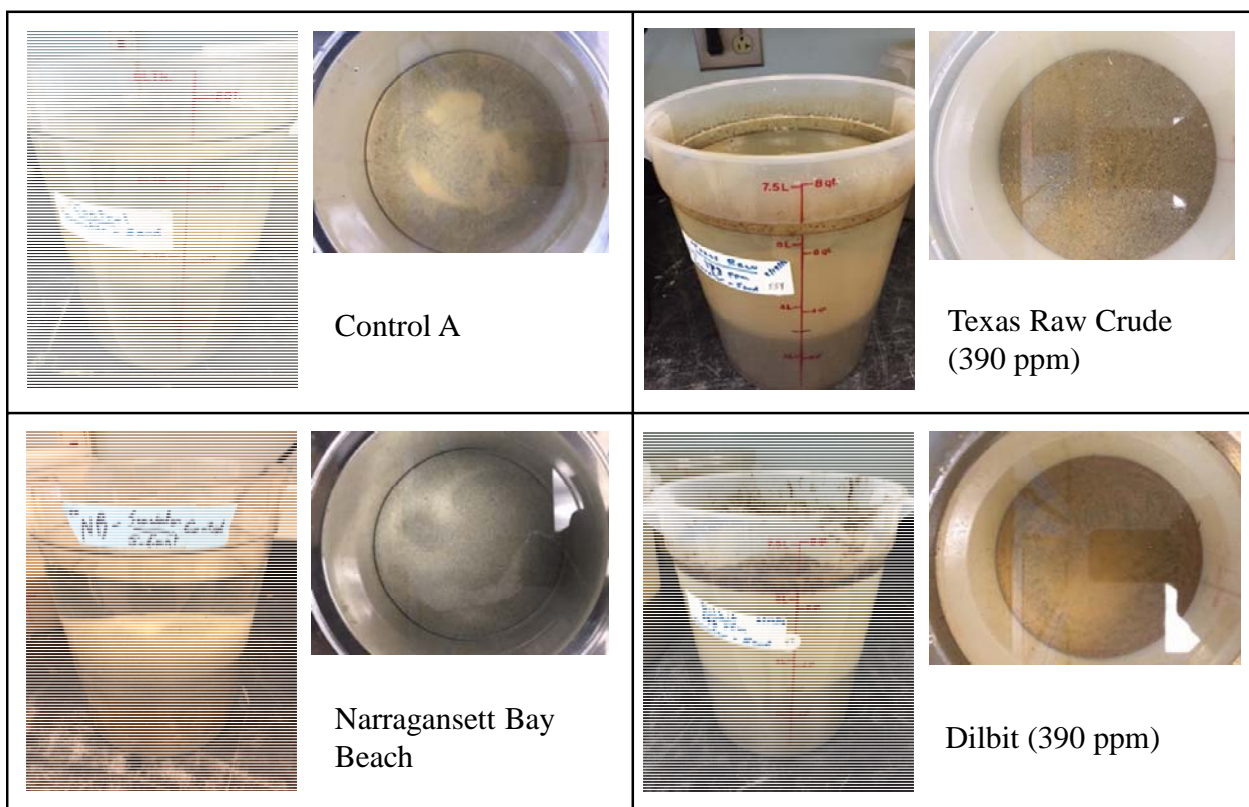


Figure D-2. Pictures (side and top views) taken on June 14, of the four treatments prepared on 19 February.

Most of the second group of 13 treatments were prepared on 19 April, by first adding crude oil to the dry sand, mixing well and then adding the seawater and remixing. The two higher concentration Dilbit treatments 12 and 13 (5000 and 10000 ppm) were prepared on 25 April. These 13 treatments (Figure D-3, Figure D-4, and Figure D-5) included:

- 1) Control B: with Commercial Sand, Seawater and no oil added.
- 2) TR2 Texas Raw Crude (Target 500 ppm) added to Seawater and Commercial Sand.
- 3) TR3 Texas Raw Crude (Target 1000 ppm) added to Seawater and Commercial Sand.
- 4) TR4 Texas Raw Crude (Target 1500 ppm) added to Seawater and Commercial Sand.
- 5) TR5 Texas Raw Crude (Target 2000 ppm) added to Seawater and Commercial Sand.
- 6) TR6 Texas Raw Crude (Target 3000 ppm) added to Seawater and Commercial Sand.
- 7) DB7 Dilbit (Target 500 ppm) added to Seawater and Commercial Sand.
- 8) DB8 Dilbit (Target 1000 ppm) added to Seawater and Commercial Sand.
- 9) DB9 Dilbit (Target 1500 ppm) added to Seawater and Commercial Sand.
- 10) DB10 Dilbit (Target 2000 ppm) added to Seawater and Commercial Sand.
- 11) DB11 Dilbit (Target 3000 ppm) added to Seawater and Commercial Sand.
- 12) DB12 Dilbit (Target 5000 ppm) added to Seawater and Commercial Sand.
- 13) DB13 Dilbit (Target 10,000 ppm) added to Seawater and Commercial Sand.



Figure D-3. DB11, the 3000 ppm Dilbit treatment, taken soon after it was prepared on 19 April.

The oil residue on the walls of the container was much less due to adding oil directly to the dry sediments first, mixing, and then adding water and remixing.

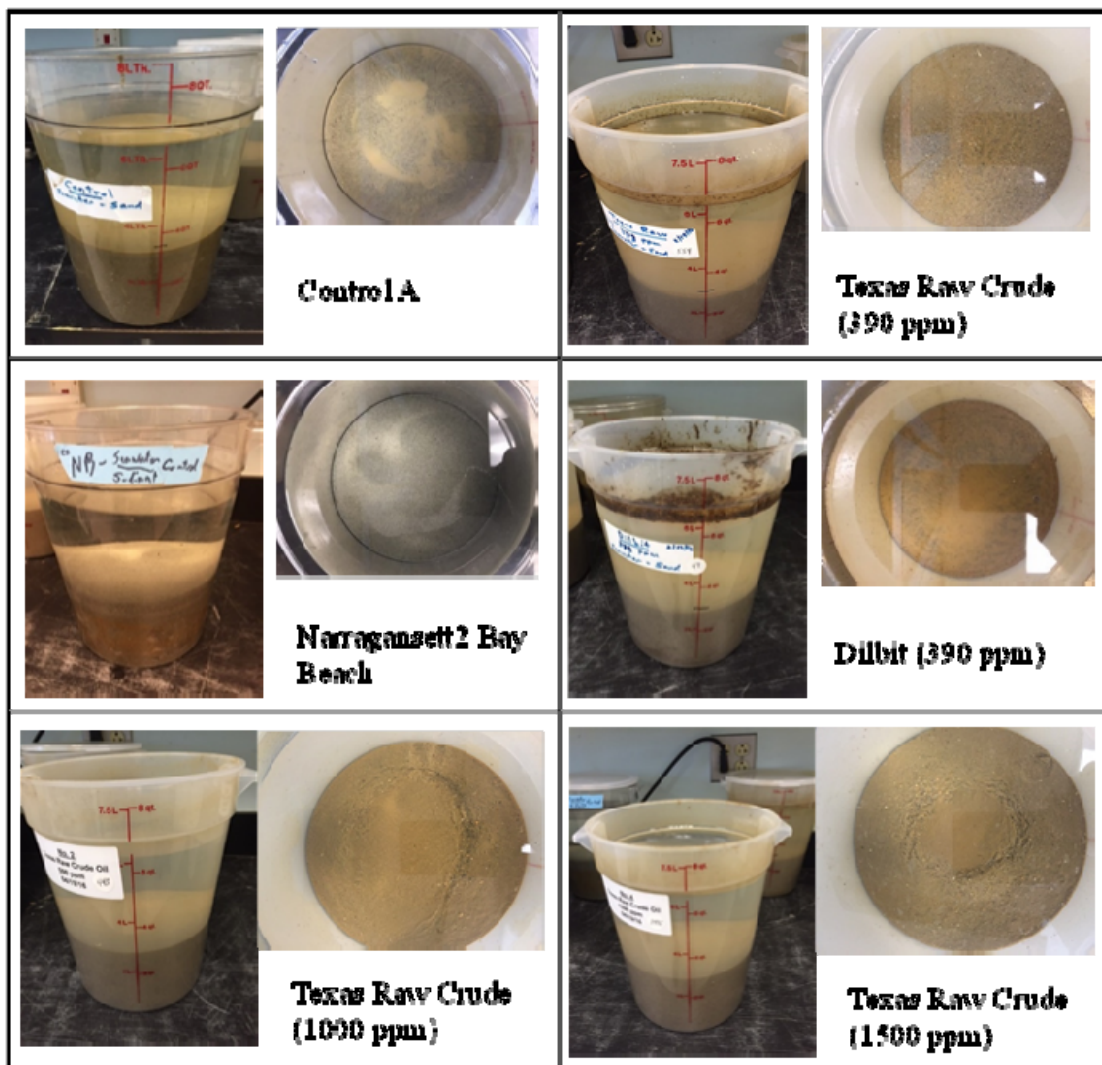


Figure D-4. Pictures taken on 14 June of the 6 Texas Raw Crude treatments prepared on 19 April.



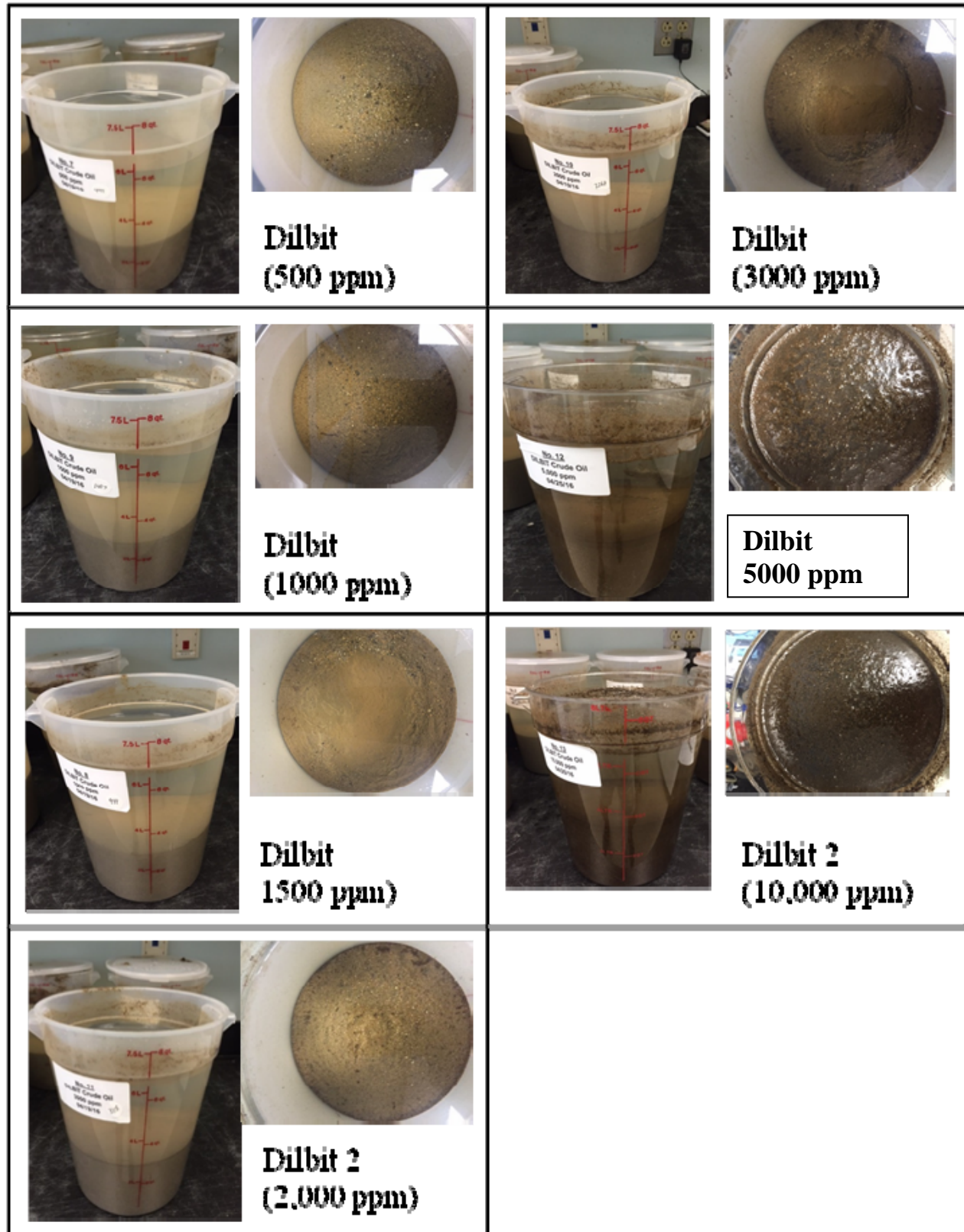


Figure D-5. Pictures taken on 14 June of the seven Dilbit treatments prepared on 19 and 25 April.

### **Additional Work Completed in June following the demonstration:**

The comparison of the six SOMS probe measurements of experimental sediments (TR 4, 5, and 6 and DB 9 and 11 – Note: DB 9 was measured in two different locations) during the demonstration on 1 June with prior measurements taken on 26 April indicating some differences in the results between April and June (range 9-47 percent less or more oil). In an attempt to understand these changes over time, the test team performed the following tests:

- 1) Test to see if there has been a systematic change in the concentration of oil that would be detected by the SOMS Probe in the surface and/or sediment pore waters of the experimental treatments since 26 April. Used the SOMS Probe to re-measure the fluorescence of the WAF of the surface and sediment pore waters of all 17 experimental treatments. These measurements were done on 6/8/16 and compared to former values.
- 2) Test to see if the TPH concentration in sediment samples from all 17 treatments on 14 June. Weighed out sediment samples for the analysis of TPH using the Dextsil PetroFlag Test Kits. Corrections were made for moisture content. These TPH measurements were completed on 16 June and compared to former values.
- 3) Test to see if remixing the oil/sediment/water mixtures, in selected treatments, would alter the concentration of oil that would be detected by the SOMS Probe in the WAF of the surface and/or sediment pore waters of the experimental treatments. The following experimental treatments were vigorously remixed and allowed to settle for a couple of days, before reanalysis with the SOMS probe: Control, TR4, TR5, TR6, DB9, DB10, and DB11. These seven treatments included the five treatments (Table I) that were measured with the SOMS Probe during the demonstration on 1 June.

### **Results from Tests 1-3:**

**Test 1 – SOMS Probe Reanalysis:** The 26 April and 8 June SOMS measurements of Texas Raw Crude in sediment pore water are compared in Figure D-6. The concentration of oil detected in the sediment pore water WAF by SOMS ranged from about 5 to 45 ppm. As evident by the graph, the data from April and June is very similar. For these five Texas Raw Crude treatments, there is no apparent systematic change in the results between the late April and early June SOMS measurements.

The 26 April and 8 June SOMS measurements of Dilbit in sediment pore waters are compared in Figure D-7. The concentration of oil detected in the sediment pore water WAF by SOMS ranged from about 0.3 to 13 ppm. As can be seen in the graph, the data from April and June are similar for two treatments (1000 and 2000 ppm) and divergent for the other three. There is much less oil detected by SOMS in the 3000 ppm treatment. Therefore, for Dilbit treatments, there is a systematic change in some of the results between the late April and early June SOMS measurements.



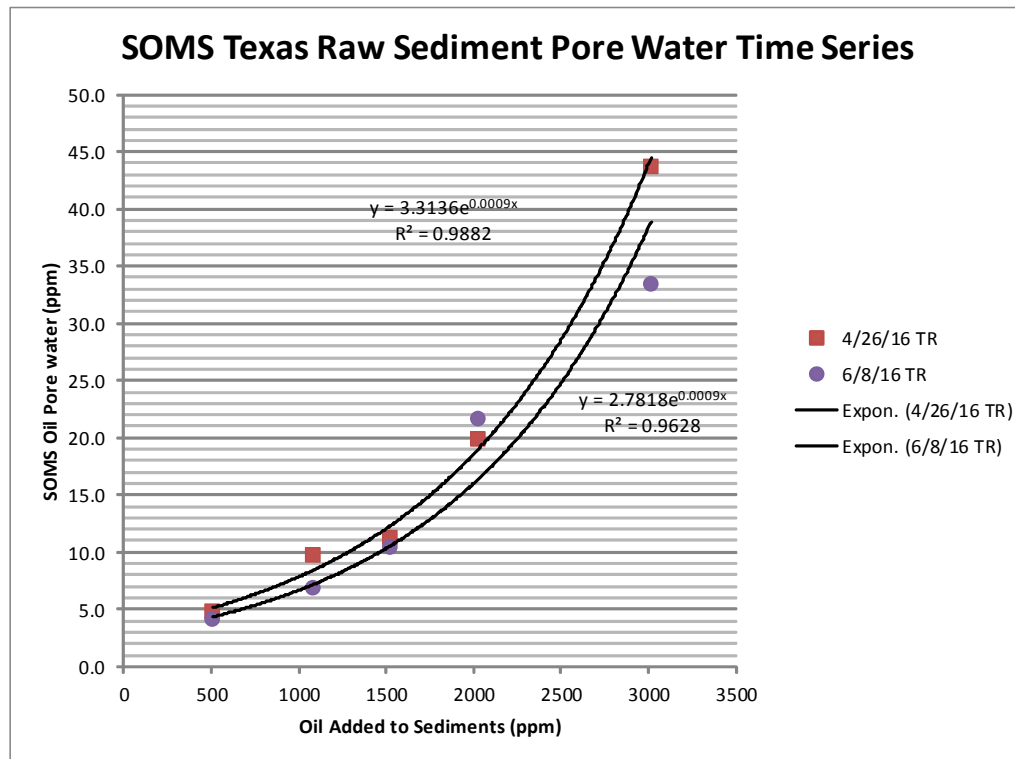


Figure D-6. Test 1, Comparison of 26 April and 8 June SOMS measurements of Texas Raw Crude in sediment pore waters.

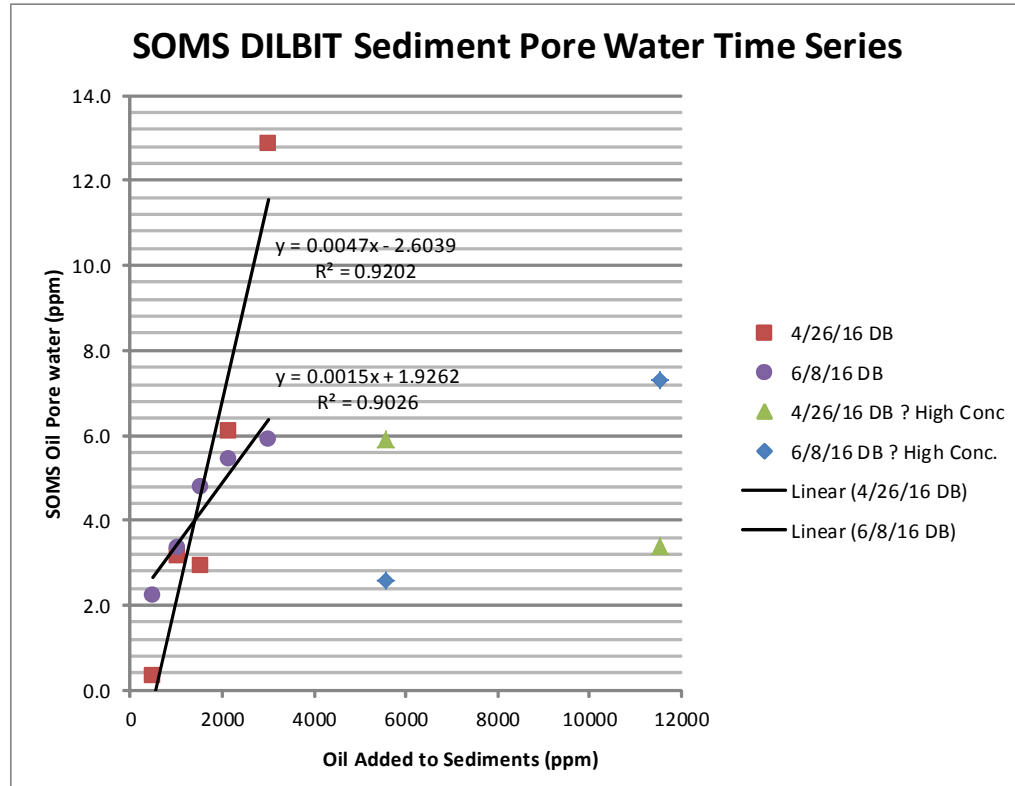


Figure D-7. Test 1, Comparison of 26 April and 8 June SOMS measurements of Dilbit in sediment pore waters.



Note the two high Dilbit concentration samples with anomalous low results in both April and June.

**Test 2 – PetroFlag Reanalysis:** The 28 April and 14 June PetroFlag measurements of Texas Raw Crude in sediment are compared in Figure D-8. The concentration of oil detected in the sediment by PetroFlag ranged from about 250 to 3500 ppm. As the below graph shows, the data from April and June is systematically different. For these five Texas Raw Crude treatments, the TPH concentration detected in the sediments decreased by about 50 percent from late April to early June.

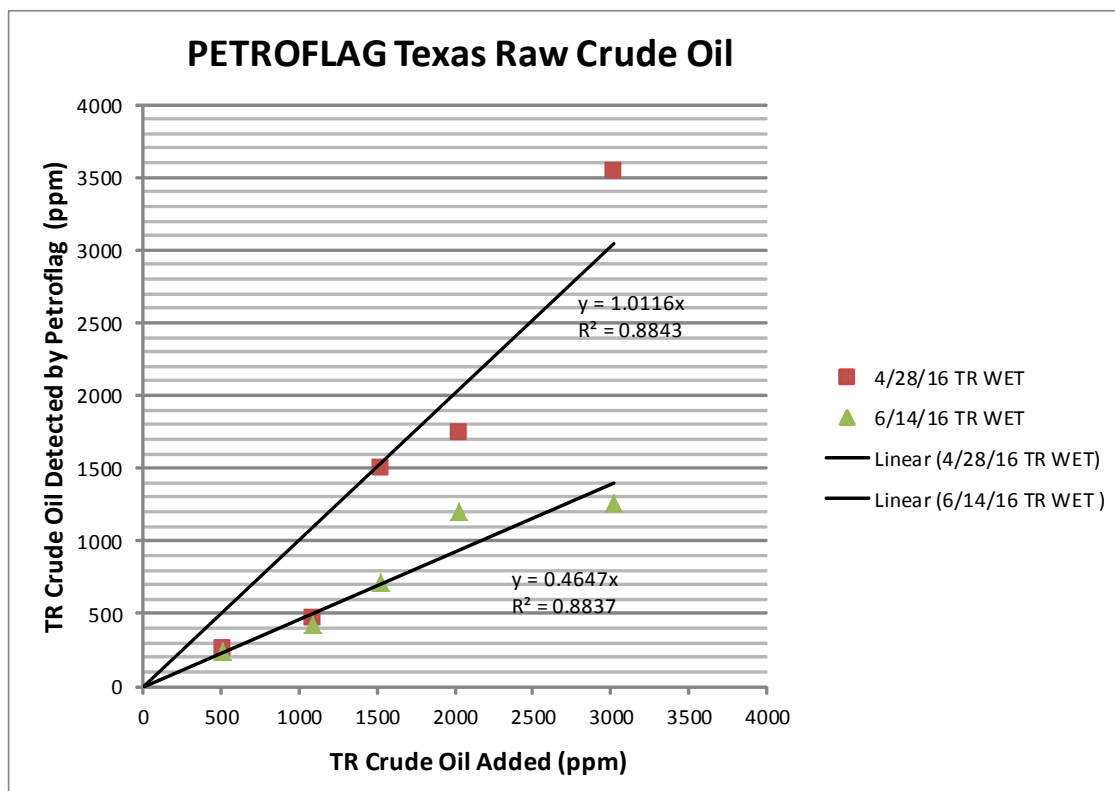


Figure D-8. Test 2, Comparison of 28 April and 14 June PetroFlag TPH measurements from the five Texas Raw Crude treatments.

The 28 April and 14 June PetroFlag measurements of Dilbit in sediment pore waters are compared in Figure D-9. The concentration of oil detected in the sediment by PetroFlag ranged from about 500 to 18,000 ppm. As the graph indicates, the data from April and June is systematically different. For these seven Dilbit treatments, the TPH concentration detected in the sediments increased by about 64 percent from late April to early June.



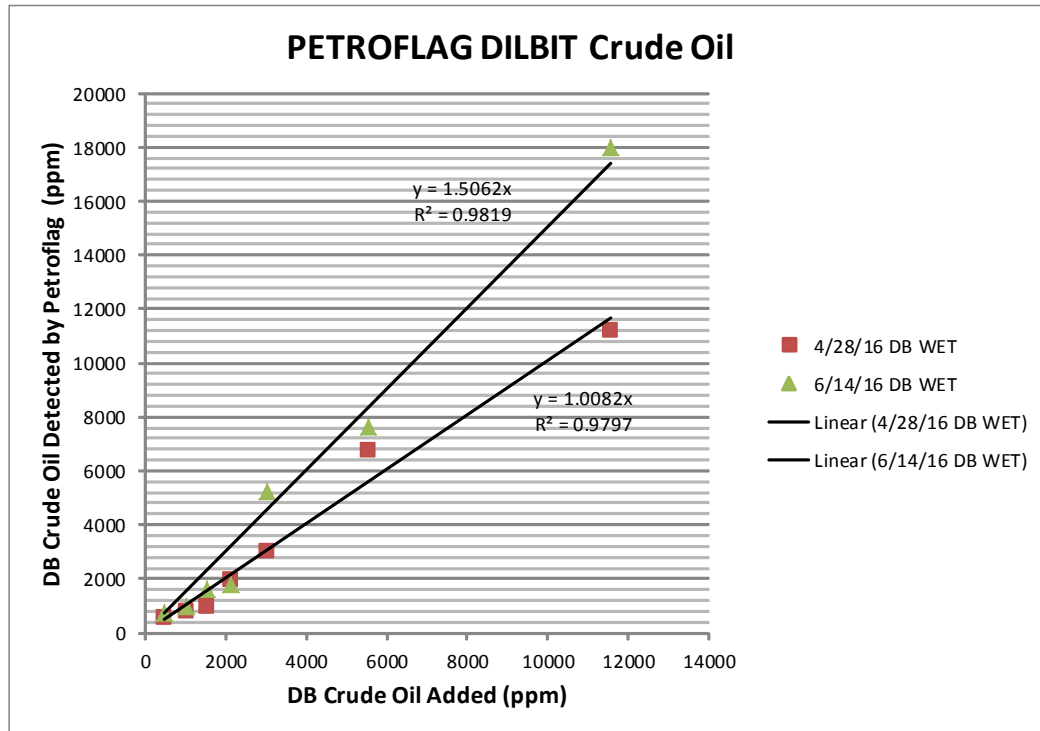


Figure D-9. Test 2, Comparison of 28 April and 14 June PetroFlag TPH measurements from the five Dilbit Crude Oil treatments.

### Evaluation of Combined Test 1 and Test 2 Results:

- In Test 1 (Figure D-6 and Figure D-7) the test team compared the concentration of oil added to the sediments to the concentration of oil detected by the SOMS Probe in the sediment pore waters, during late April and early June, for five Texas Raw Crude and seven Dilbit experimental treatments.
- In Test 2 (Figure D-8 and Figure D-9) the test team compared the concentration of oil added to the sediments to the concentration of oil detected in the sediment by the PetroFlag TPH detection method, during late April and early June, for five Texas Raw Crude and seven Dilbit experimental treatments.
- In Figure D-613 and Figure D-714, the test team combined these two sets of results for the five Texas Raw Crude and seven Dilbit experimental treatments. The TPH concentration detected in the sediments by the PetroFlag method in late April and early June are compared to the concentration of oil detected using the SOMS Probe in the sediment pore waters of each treatment.
- The plotted data for the Texas Raw Crude treatments (Figure 14) indicates that there was more oil detected by SOMS in the pore waters, relative to the PetroFlag TPH measured sediment oil contents, during early June than in late April.
- Figure 14 indicates that the same amount of oil was detected by SOMS in the pore waters, relative to the PetroFlag TPH measured sediment oil contents, during early June than in late April. The two high Dilbit concentration samples had anomalously low results in both April and June.
- Test 3 – SOMS Probe Reanalysis After Remixing: During the demonstration on 1 June, the question was raised about what would happen if the experimental treatments were to be remixed and then re-analyzed using the SOMS Probe. Seven experimental treatments (Figure D-10) were selected to answer the remixing question: Control B and Texas Raw Crude ~1500 ppm, ~2000 ppm, ~3000 ppm and Dilbit ~1500 ppm, ~2000 ppm, ~3000 ppm treatments. The comparative results are shown in Figure 15 for the Texas Raw Crude and in Figure 16 for the Dilbit Treatments.



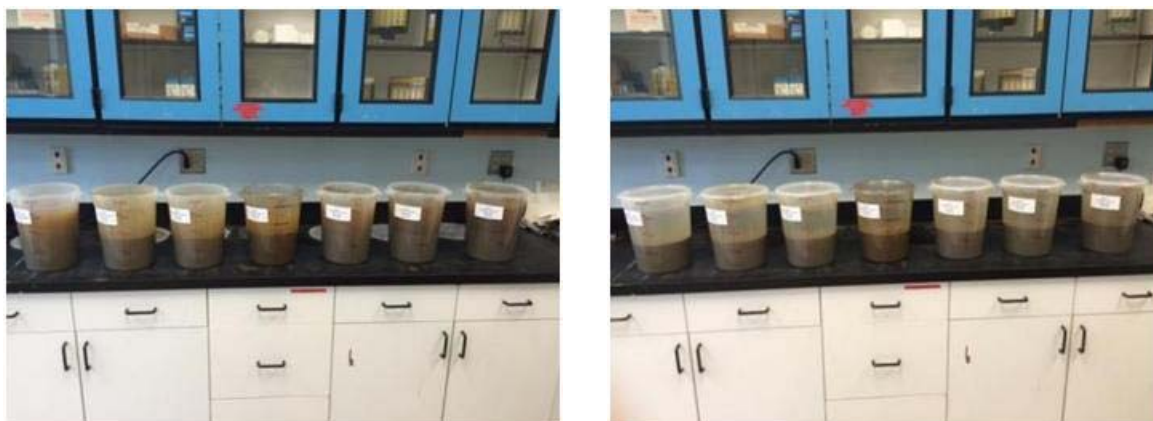


Figure D-10. Before (left) and after (right) remixing of seven experimental treatments. The remixed treatments are still settling out in the picture on the right. Left to right; Control B and Texas Raw Crude ~1500 ppm, ~2000 ppm, ~3000 ppm and Dilbit ~1500 ppm, ~2000 ppm, ~3000 ppm treatments. The treatments settled for two days before being re-measured with the SOMS Probe.

**Evaluation of the Test 3 Remixing Results:** The comparative June SOMS Probe measurements (Figures 15 and 16) of the sediment pore water oil contents, before and after remixing seven of the experimental treatments, were surprisingly similar. This was particularly true of the 8 June (before remixing) and 14 June (after remixing) measurements. The results from the SOMS Probe measurements obtained during the 1 June demonstration are also included in the two graphs, and agree fairly well with the post-remixing SOMS Probe readings.

### **Discussion of SOMS and PetroFlag Experimental Time-Series Observations:**

This section addresses questions related to the repeatability of the SOMS and Petro-Flag measurements over time for the 17 experimental treatment containers containing mixtures of sediment, seawater and different concentrations of crude oil (Texas Raw Crude and Dilbit). If anomalous oil measurement results are observed over time, the two questions to be answered are:

- 1) Are the changes due to the PetroFlag or SOMS oil measurement techniques?
- 2) Are they actual changes, occurring over the time span of observations (two to four months), in the crude oil distribution or concentration in the sediment, water and air phases laboratory experimental containers.

To address these questions:

- 1) The time-series of oil measurements on these 17 treatments, by both the PetroFlag and SOMS methodologies, was reviewed.
- 2) Some additional experiments (Tests 1, 2, and 3) have also been conducted, to help evaluate the potential variation in SOMS and PetroFlag measurements over time.

The experimental laboratory scale plan and approach followed involved carefully preparing a series of experimental treatments (17) in plastic containers (approximately eight liter) containing sediment (4.5 kg), water (4.5 kg) and crude oil (0-50 g), with a goal to obtain a defined concentration gradient (ppm range) of crude oil in the sediment phase. This was a simple idea, but as it turned out, a complex task. The test team did not have an objective goal or the ability to create oil/sediment/water mixtures that would maintain the same oil concentrations in the various phases, over time.



## Underwater Sediment Sampling Research

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The concentration of crude oil in the sediments was experimentally defined by two methods by knowing the weight of crude oil added to the sediment and precisely measuring the concentration of total petroleum hydrocarbons (TPH) in a sediment sample using the Dexsil PetroFlag TPH test kit.

After the crude oil (a complex mixture of organic chemicals) was added to and homogeneously mixed/blended with the dry sediment, seawater was added and the water and sediments were homogeneously mixed a second time. During (and after) these mixing events, the crude oil components had an opportunity to end up where they preferred to be, based upon their physiochemical properties (i.e. solubility, hydrophobic or hydrophilic nature, viscosity, volatility, etc.).

The aggressive mixing imparted energy to the oil/sediment/water mixtures, and essentially set up a multi-phase system that was not in physio-chemical equilibrium. After the mixing stopped, and the containers sat on the bench for two to four months, the chemical components of the oil were free to weather, diffuse and migrate, at some rate, over time, towards a more equilibrated state.

After the treatment containers were mixed and allowed to settle for a couples of days, the SOMS Probe could be used to take measurements of the oil content of the surface water layer (location # 4) and the sediment pore waters (location # 2). Representative core samples could also be taken (2-10 gram subsamples) for measuring the sediment oil contents (location # 1) using the PetroFlag test kit. Seventeen experimental treatments were prepared, four on 19 February and thirteen on 19 April. Since they were initially created, the water, sediment-water interface and sediments of these experimental containers were disturbed by being sampled a number of times for either getting a PetroFlag core sample, or making an in situ measurement with the SOMS probe. It seems likely that the sediment penetrating PetroFlag core sampling and SOMS Probe measurements would also allow some exchange, concentration, and or dilution of oil chemical constituents between the sediments, sediment pore waters and surface waters.



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### APPENDIX E. ROV DESIGN ATTRIBUTES

Desired design attributes for the ROV are described here, rather than areas for development, because the ROV will be a Commercial-off-the-shelf (COTS) item.

Marine ROVs in use today can be generalized into two widely different groups: small observation units and large construction-type units. Observation units are used to see things underwater in place of divers. They operate in the water column propelled by thrusters, and are equipped, at a minimum, with lighting and cameras, and are referred to (Marine Technology Society, n.d.) refers to these observation units as Micro ROVs (<100m depth) or Mini ROVs (<300m depth). Functional capability beyond inspection is often very limited. For the current project, there is a concern that thrusters might upset the sediments under study.

Larger ROVs with great depth and functional capability are produced for work in undersea operations, such as cable trenching and oil field construction. These include, for example, heavy work class ROVs working in depths up to 3500m and trenching/burial ROVs working at depths up to 6000m. These ROVs are generally bottom crawlers, propelled by wheels or tank-like tracks, and include additional equipment such as manipulators, water samplers, sonar capability, or other work packages. An essential design element is weight (negative buoyancy), which is required to hold the ROV on the bottom firmly, as the ROV interacts with the bottom to perform its functions.

In between the two extremes described above are a growing number of ROVs that augment the functionality of observation ROVs in a small package. For example, ROVs have been developed to clean biofouling from ship hulls. Small ROVs with bottom crawler capability are not common, however, one small hybrid commercial ROV developed by 1Robotics combines thrusters with bottom crawler propulsion (Figure E-1). This type of ROV may provide a platform for future SOMS testing.



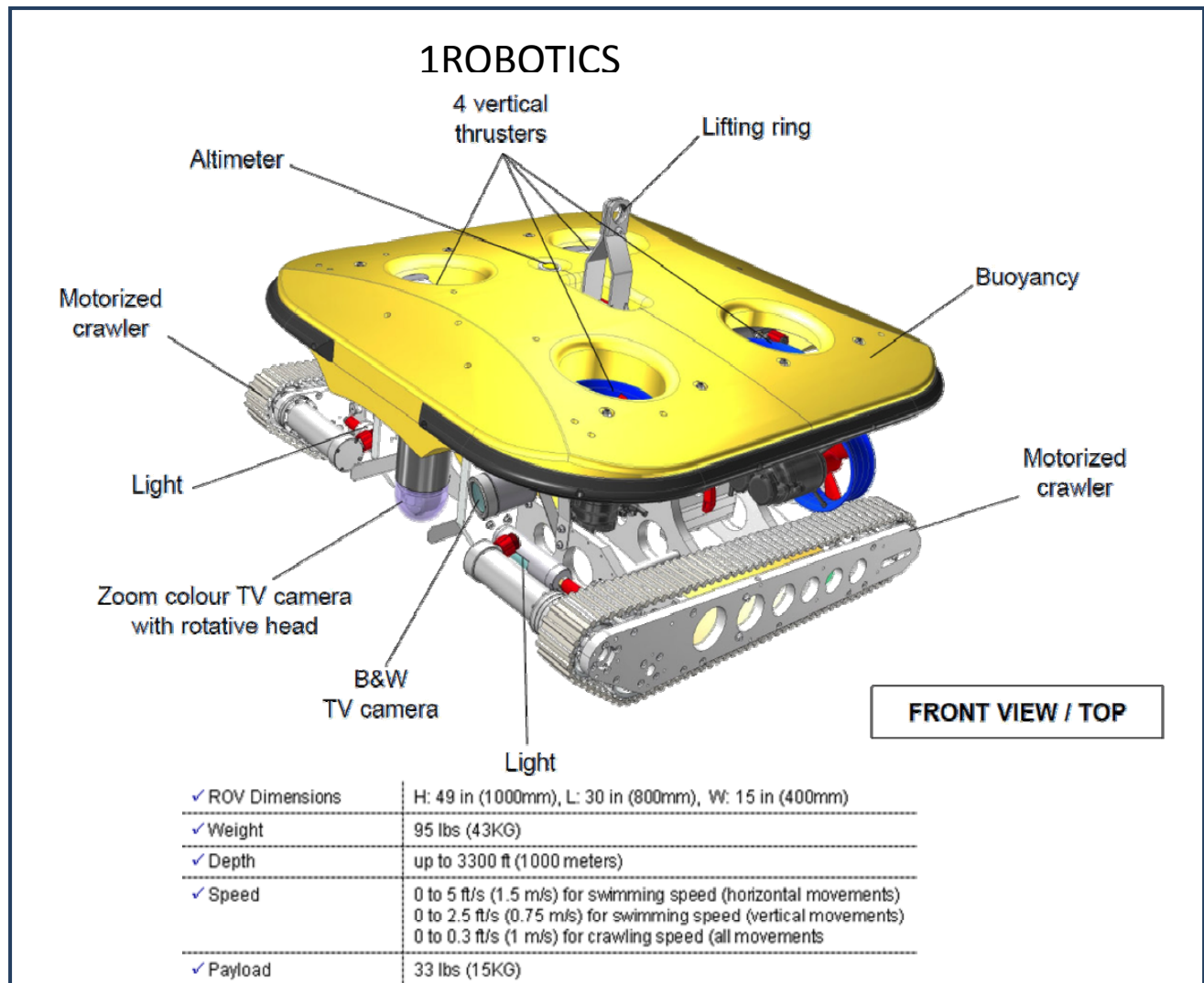


Figure E-1. Small hybrid ROV.

Attributes of an ROV that might be used to deploy the SOMS are listed in Table E-1 in order of importance as judged by the test team.

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Table E-1. Desirable ROV attributes.

| No. | Attribute        | Need  |
|-----|------------------|---|
| 1   | SOMS Integration | SOMS integration includes a mounting location and method, as well as interfaces with the ROV that might be required or desired to meet requirements, such as power or control. The preferred industry approach is to use a removable skid or auxiliary work package to mount the SOMS. Mounting configuration will affect balance, speed, power and other design aspects on the ROV. Typical ROV design mounts heavier items towards the bottom and lighter elements, such as the buoyancy canister up high to increase stability. A lower mounting is also desirable for the SOMS to facilitate the probe insertion and depth measurement functions. |
| 2   | Ballast/buoyancy | Size and weight should be such that the required pressure is exerted at the probe insertion point. Size and weight should be such that it will remain stable in a 0.5 knot current on the bottom during the measurement process. Reserve stability is required to offset the current force on mounted systems such as SOMS and on cables running to the surface platform. In some designs where the ROV must operate on the bottom, weight may be simulated using vertical thrusters pushing the ROV downward.  |
| 3   | Mobility         | Ability to move in a forward direction without disturbing sediment in front of it (potential sampling area). ROV should be able to reverse direction and turn to avoid objects, and should have sufficient ground clearance to move over small obstacles such as rocks, shells, etc. This suggests a "crawler" ROV type.  |
| 4   | Cameras          | Some combination of TV, video, or still cameras is needed to provide situational awareness. In particular a camera that can view from a distance downward can help identify a clear area to land on the sediment to take TPH readings. A forward camera can help avoid hitting objects. Trainable cameras are useful to allow changing a viewing area without moving the ROV.   |
| 5   | Lighting         | Lighting must complement the camera setup. In general, high illumination increases backscatter but may be required for color cameras. Low illumination may provide better long-range views and could be coupled with a low light level camera.  |
| 6   | Power            | Provide sufficient power to the SOMS. This power may be provided separately to the SOMS using batteries or via a power cable, or it could be provided by a compatible power supply from the ROV.  |
| 7   | Other Systems    | For an implemented operational system, capacity to integrate other systems, such as a sediment sample grabber, would be desirable. This may not be needed for a working SOMS that will be used for field test purposes.   |





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